Chem Factsheet

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σ - and π - Bonds and the Structure of Benzene

To succeed in this topic you need to understand:
- atomic structure (Factsheet 1);
- bonding (Factsheet 5).
- calculation of enthalpy changes using average bond energies (Factsheet 8)

After working through this Factsheet you will:
- understand the difference between σ- and π-covalent bonds;
- know that the carbon-carbon double bond in alkenes comprises a σ- and a π-bond;
- know that the benzene ring contains six identical carbon-carbon bonds;
- understand the nature of these bonds;
- know that the π-bond electrons in benzene are delocalised;
- know that delocalisation leads to enhanced stability;
- be able to calculate the stabilisation energy of benzene.

Single covalent bonds

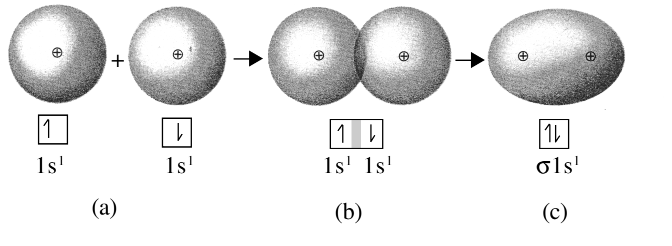
A covalent bond is formed when a pair of electrons, one from each atom, is shared between them. Both electrons must originally be in singly occupied atomic orbitals.

Remember *- An atomic orbital (AO) is a three-dimensional region of space around the nucleus of an atom where there is a high probability of finding an electron. An atomic orbital may be:*

- *vacant, i.e. empty, symbolised* ☐
- *singly occupied, i.e. containing one electron, symbolised* [↿]
- *fully occupied, i.e. containing a pair of electrons with opposite spin, symbolised* [⇅]

When the atoms approach each other, their singly occupied orbitals overlap and interact to give a molecular orbital (MO) which surrounds both nuclei and holds both electrons. Fig. 1 shows the fomation of a *σ-molecular orbital* or *σ-bond* (pronounced 'sigma bond') between two hydrogen atoms.

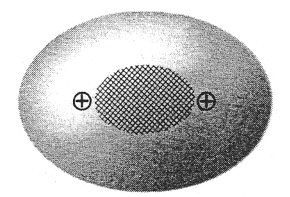
Fig. 1. Formation of the H-H bond



(a) The approach of two hydrogen atoms possessing s-orbital electrons with opposite spins
(b) Overlap of atomic orbitals
(c) The resultant molecular orbital

A great deal of heat is evolved as the two atoms combine together, showing that a hydrogen molecule is more stable than two separate hydrogen atoms. It has lower enthalpy value. Stability results from the high electron density that exists between the two nuclei (Fig.2).

Fig. 2 The region of a hydrogen molecule where there is a high probability of locating the two electrons is between the two nuclei

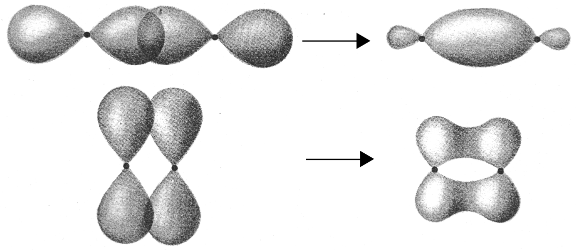


The two hydrogen atoms are strongly bonded together because:
- *the shared pair of electrons reduces repulsion between the two nuclei;*
- *the positive nucleus of each atom is attracted to the neagtive charge density betwen them..*

σ- and π- bonds

s-Orbitals are spherically symmetrical about an atomic nucleus and there is only one way in which they can overlap. p-Orbitals, however, are dumb-bell shaped, and overlap could conceivably occur in two ways (Fig. 3).

Fig. 3 Possible modes of overlap of p-orbitals



(a) Head-on overlap of p-orbitals, leading to a σ-bond (σ-MO)
(b) Sideways overlap of p-orbitals, leading to a π-bond (π-MO)

Wherever possible - and this applies to molecules such as F_2 and Cl_2 - there is head-on approach of p-orbitals because this leads to a greater degree of overlap and hence greater stability.

The formation of a F_2 or Cl_2 molecule is therefore represented by Fig. 3(a). Notice that the shape of a σ-bond, like that of the σ-bond in the H_2 molecule, stems from the fact that electron density is greatest between the two atomic nuclei. The overlapping lobes of the AOs are thus increased in size, while the outer lobes are correspondingly decreased.

Double covalent bonds

In certain circumstances p-orbitals can only overlap in a sideways manner, to give relatively weak π-bonds. This is what happens in the formation of the ethene molecule, $CH_2{=}CH_2$.

Formation of the σ-framework of ethene

Carbon in its *ground state* (i.e. most stable electronic state) has the configuration: $1s^2, 2s^2, 2p^2$

This means that the atom has two unpaired electrons:

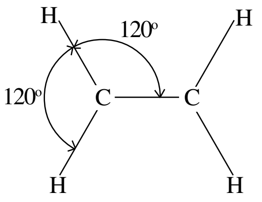
	1s	2p
Ground state	⇅	↑ ↑ ☐

This in turn would lead to a covalency of 2, i.e. the ability to form two covalent bonds. However, if energy is available, one of the 2s electrons can be promoted to a vacant 2p orbital:

	1s	2p
Excited state	⇅	↑ ↑ ↑

In this *excited state* carbon has four unpaired electrons, corresponding to its well known covalency of 4. In forming ethene, two carbon atoms each use their 2s and *two* of their 2p electrons to give the *σ-framework* of the molecule (Fig.4), so-called because all the bonds are σ-bonds.

Fig. 4 σ-Framework of the ethene molecule

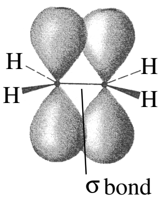


> ***Exam Hint -*** *There is no need to study the formation of the σ-framework in detail, but you do need to know that it is trigonal planar with bond angles of 120° about each carbon atom.*

Formation of the π-bond in ethene

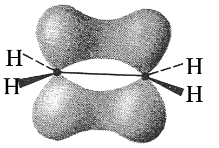
After forming the σ-framework, each carbon atom has an unpaired 2p electron 'left over'. These electrons occupy orbitals which lie perpendicular to the plane of the σ-framework, and which are sufficiently close together to overlap slightly in a sideways manner both above and below the plane (Fig. 5).

Fig. 5 Sideways overlap of $2p_z$ AOs in the ethene molecule



Overlapping leads to interaction, and the result is a π-bond which holds both the electrons. It consists of two lobes, one above and the other below the plane, each with a shape that is derived from those of the contributing AOs (Fig. 6).

Fig. 6 The π-MO in the ethene molecule



> ***Remember -*** *Both electrons of the π-bond exist in both lobes. Do not make the mistake of thinking that each electron is restricted to one lobe.*

The strength of any covalent bond depends on the degree of overlap of atomic orbitals as the molecular orbital is formed. Because, in ethene, there is little sideways overlap of π-orbitals, the p-bond is relatively weak.

> ***Remember***
> - *Although the carbon-carbon double bond is printed C=C, the two covalent bonds are different from each other. One is a σ-bond and the other, which exists above and below the plane of the σ-framework, is a π-bond.*
> - *The π-bond is much weaker than the σ-bond. This is the one that is broken during addition reactions.*

The C-C single bond in alkanes is **very** difficult to break because of the strength of the σ-bond. The electron density is **between** the atoms. The π-bond present in the C=C double bond in alkenes is

- weak
- gives negative charge density above and below the C-C σ-bond which attracts **electrophiles**.

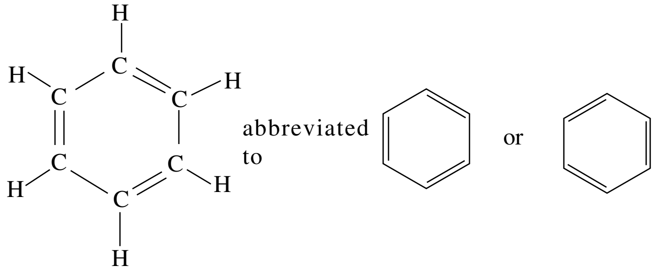
In addition reactions of alkenes, the strong σ-bond in the molecule is **not** broken, e.g.

$$\underset{\substack{\text{double bond}\\(\sigma\text{ and }\pi\text{-bonds})}}{CH_2{=}CH_2} + H_2 \rightarrow \underset{\substack{\text{single bond}\\(\sigma\text{ -bond only})}}{CH_3{-}CH_3}$$

Bonding in benzene

Benzene has the molecular formula C_6H_6. August Kekulé (1865) proposed a structural formula in which the six carbon atoms were linked together in a regular, planar hexagon (the 'benzene ring') by alternate double and single bonds (Fig. 7).

Fig. 7 The Kekulé formula of benzene



Although Kekulé's formula was accepted for many years, evidence accumulated showing that it was not entirely correct. Measurements of bond lengths were particularly damning:

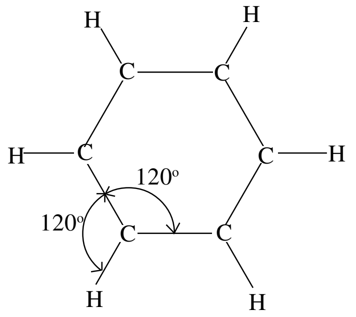
	Length/nm
C-C single bond	0.154
C-C double bond	0.134
C-C bond in benzene	0.139

All C-C bonds in benzene were found to have a length of 0.139 nm. This suggested that they had an identical character, between that of a single bond and that of a double bond. The Kekulé theory was eventually replaced by the molecular orbital theory, according to which the benzene molecule contains σ- and π-bonding, similar to that in ethene.

Formation of the s-framework of benzene

In forming the σ-framework (Fig. 8), each carbon atom, as in ethene, uses its 2s and *two* of its unpaired 2p electrons. (As for ethene, details are not required by current A-level specifications.)

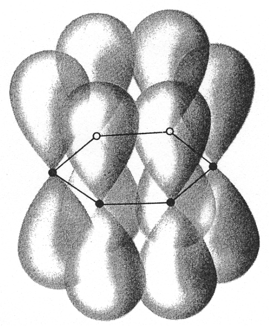
Fig. 8 σ-Framework of the benzene molecule



Formation of the π-bond in benzene

All six carbon atoms have their remaining singly occupied 2p orbitals lying perpendicular to the plane of the σ-framework. They are close enough together to overlap uniformly all around the ring (Fig. 9).

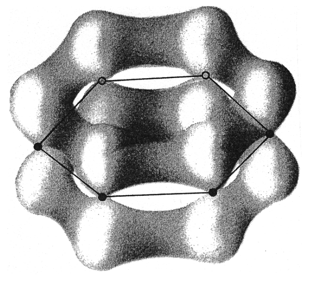
Fig. 9 Uniform overlap of six $2p_z$ AOs, perpendicular to the plane of the benzene σ-framework

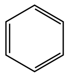
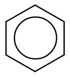


Interaction gives a π-bond holding the six electrons.* It consists of two lobes, one above and one below the σ-framework. As always, the shape of the molecular orbital is derived from the shapes of the contributing atomic orbitals (Fig. 10).

> * Strictly, this is wrong: no orbital can hold more than two electrons. In fact, *three* π-molecular orbitals are formed, of different shapes and with two electrons in each, but at A-level it is assumed that all six electrons occupy the π-orbital shown here.

Fig. 10 The π- molecular orbital in the benzene molecule



> *Because of the symmetry of the σ-framework, the π-orbitals cannot overlap in pairs to give alternate double and single bonds.*
>
> *Consequently, the old symbol for benzene,* 
>
> *has been replaced by a new one,*  *, in which the circle represents the π- bond.*

Delocalisation of π-electrons

> - *If the benzene molecule had three separate π-bonds, as implied by the Kekulé formula, the π-electrons would be* localised*, i.e. confined to the three regions between the doubly bonded carbon atoms.*
> - *Because there is a single π-bond extending all around the molecule, the π-electrons are* delocalised*, i.e. not restricted to certain localities but dispersed among all six carbon atoms.*

Delocalisation energy

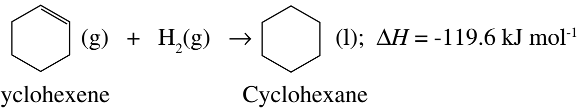
Delocalisation of electrical charge always leads to an increase in stability. In the case of a metal sphere, if electrons were to be concentrated at one point on its surface, they would repel one another and immediately become uniformly distributed over the entire surface to give a more stable arrangement.

> *Benzene, because of its delocalised π-bond, is more stable than it would be if it had three localised π-bonds between alternate pairs of carbon atoms.*

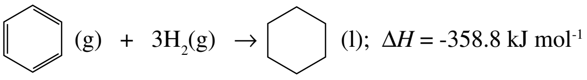
A question often asked in examinations is this: how much more stable is benzene as a result of delocalisation? A figure can be calculated from enthalpies of hydrogenation or combustion.

Calculation of delocalisation energy from enthalpies of hydrogenation

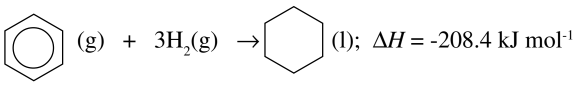
The molar enthalpy of hydrogenation of cyclohexene, a six-membered ring compound with one localised π-bond, is -119.6 kJ mol^{-1}:


$(g) + H_2(g) \rightarrow$ $(l);\ \Delta H = -119.6\ kJ\ mol^{-1}$

Consequently, if benzene were a cyclic compound with three localised π-bonds, its molar enthalpy of hydrogenation would be 3(-119.6) = -358.8 kJ mol^{-1}:


$(g) + 3H_2(g) \rightarrow$ $(l);\ \Delta H = -358.8\ kJ\ mol^{-1}$

Actual benzene has one delocalised π-bond and the experimental value of its molar enthalpy of hydrogenation is -208.4 kJ mol^{-1}:

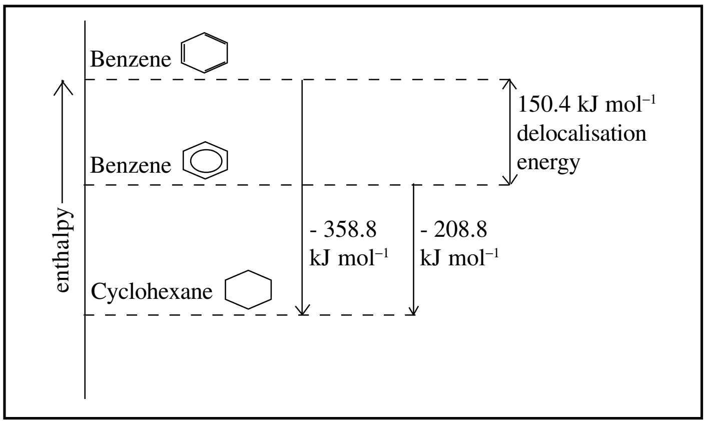

$(g) + 3H_2(g) \rightarrow$ $(l);\ \Delta H = -208.4\ kJ\ mol^{-1}$

The difference between these values, 150.4 kJ mol^{-1}, is known as the *delocalisation energy* or *stabilisation energy* of benzene.

> *Because of the delocalisation of its π-electrons, benzene is at a lower energy level than it would otherwise be to the extent of 150.4 kJ mol^{-1}.*

Fig. 11 will help you to understand this.

Fig. 11 Enthalpy diagram to show the delocalisation energy of benzene



Delocalisation is not confined to benzene, but occurs in all *conjugated compounds*, i.e. those with alternating double and single bonds. An example is buta-1,3-diene:

$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2$$

While double bonding is most marked between C_1 and C_2, and between C_3 and C_4, the bond between C_2 and C_3 also has a certain amount of double bond character as a result of delocalisation.

Practice Questions

1 (a) What atomic orbitals contribute to the covalent bond of the HF molecule?
(b) Draw a diagram to show the mode of overlap of these atomic orbitals.
(c) Is the resulting molecular orbital a σ-bond or a π-bond?

2 Why is the double bond in ethene **not** twice as strong as the single bond in ethane?

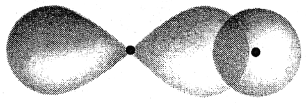
3 Briefly explain why ethene is more reactive than ethane, even though the carbon-carbon bond is stronger.

4 Why does HBr react with ethene but not with benzene?

5 The molar enthalpy of combustion of benzene is -4866 kJ mol^{-1}. Use this information and the following average bond enthalpies (all in kJ mol^{-1}) to estimate the delocalisation energy of benzene.
C-C = 348; C=C = 612; C-H = 412; C=O = 743; O=O = 496; O-H = 463.
[$C_6H_6 + 7\frac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O$]

Answers

1 (a) 1s orbital of hydrogen and a singly occupied 2p orbital of fluorine.
(b)



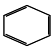
Note. Diagram must show end-on overlap of the p-oribtal
(c) σ-bond.

2 The double bond comprises a σ-bond and a π-bond, whereas a single bond consists of a σ-bond only. Electrons in a π-bond are located above and below the internuclear axis, making less contribution to the reduction of internuclear repulsion / so that the bond is weaker.

3 In most reactions of ethene only the π-bond is broken. This is weaker than the σ-bond in ethane, and the electrons, since they lie beyond the internuclear axis, are more susceptible to electrophilic attack.

4 HBr is an electrophilic (electron seeking) reagent, which is strongly attracted to the π-bond electrons of ethene. In benzene, the π-electrons are delocalised, so that the electron density between any two adjoining carbon atoms is lower than it is in ethene. Electrophilic reagents are therefore less strongly attracted.

5 Answer should be based on the combustion of 'Kekulé benzene':


$+ 7\frac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O$

ΔH *for bond breaking*				ΔH *for bond formation*			
3 C-C	3(+348)	=	+1044	12 C=O	12(-743)	=	-8916
3 C=C	3(+612)	=	+1836	6 O-H	6(-643)	=	-2778
7½ O=O	7½(+496)	=	+3720		Total	=	-11694 kJ mol^{-1}
	Total	=	+6600 kJ mol^{-1}				

Overall Δ*H*, i.e. enthalpy of combustion of 'Kekulé benzene', = +6600 - 11694 = -5094 kJ mol^{-1}.
∴ delocalisation energy = 5094 - 4866 = 228 kJ mol^{-1}

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