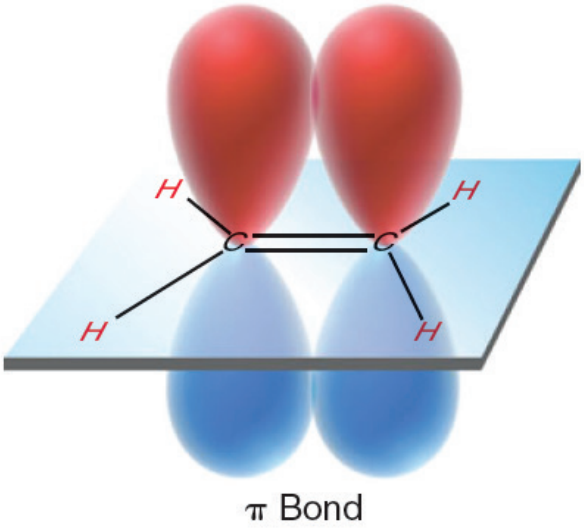
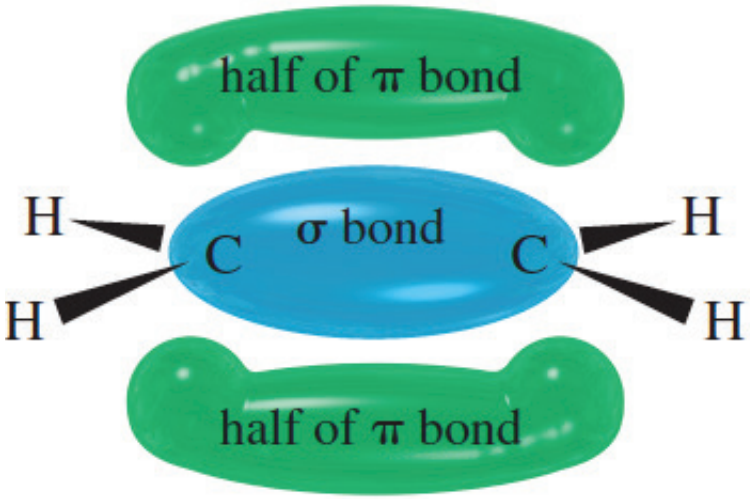
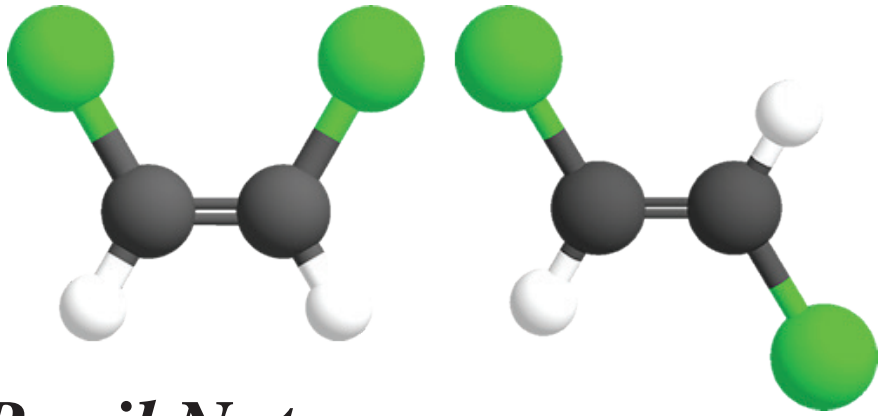
Unit 3 - Organic Chemistry

3.1 Molecular Structure

Molecular Orbitals
Molecular Structure
Stereochemistry







Pupil Notes
Learning Outcomes
Questions& Answers

Permeating Aspects

3.1.1 *Equations can be written for the following reaction types and, given equations, these reaction types can be identified.*

substitution *addition* ***elimination*** *condensation*

hydrolysis *oxidation* ***reduction***

3.1.2 ***Homolytic fission*** *involves the breaking of a bond where the two shared electrons are redistributed equally to form particles with unpaired electrons called* ***radicals***.

3.1.3 ***Heterolytic fission*** *involves the breaking of a bond where the two shared electrons go to just one atom to form charged particles.*

3.1.4 *The* ***polarity*** *of the bond along with the ability to* ***stabilis****e charges will determine the charges formed.*

3.1.5 *A carbon with a positive charge is called a* ***carbocation*** *(also called a* ***carbonium*** *ion) while a negatively charged carbon (less common) is called a* ***carbanion***.

3.1.6 ***Electrophiles*** *(electron seeker) are atoms or groups of atoms deficient in electrons and are attracted to groups which can donate electrons.*

3.1.7 ***Nucleophiles*** *(nucleus seeker) are atoms or groups of atoms rich in electrons and are attracted to positively charged centres.*

Structures - Molecular Orbitals

3.1.8 *In* ***Alkanes*** *the carbon atoms use all 4 atomic orbitals (2s, $2p_x$, $2p_y$ and $2p_z$) to form 4 hybrid sp^3 molecular orbitals (tetrahedral).*

3.1.9 *The sp^3 orbitals overlap* ***end-on*** *to form 'normal'* ***sigma*** *(σ) bonds where the electron pair lie between the two nuclei.*

3.1.10 *The bonds in alkanes are non-polar and are resistant to attack by both electrophiles and nucleophiles, but radicals will be able to cause reaction*

3.1.11 *Alkanes undergo* ***substitution*** *reactions with chlorine and bromine by a chain reaction mechanism.*

3.1.12 *The* ***chain reaction*** *includes the following steps*

(i) ***initiation*** *by homolytic fission to produce radicals*
(ii) ***propagation***
(iii) ***termination***

3.1.13 *In* ***Alkenes*** *the carbon atoms use only 3 atomic orbitals to form 3 hybrid sp^2 molecular orbitals (trigonal planar).*

3.1.14 *The sp^2 orbitals overlap* ***end-on*** *to form 'normal'* ***sigma*** *(σ) bonds where the electron pair lie between the two nuclei.*

3.1.15 *The unused p orbitals overlap* ***sideways*** *to form* ***pi*** *(π) bonds where the electron pair lie out to the side.*

3.1.16 *The* ***pi*** *(π) bond is weaker than the* ***sigma*** *(σ) bond and the electron rich region makes it susceptible to electophilic attack.*

3.1.17 *All multiple bonds (eg C=O , C≡C) are a combination of one* ***sigma*** *(σ) bond and at least one* ***pi*** *(π) bond.*

3.1.18 *The backbone of a benzene ring are the sp^2 hybrid orbitals overlapping to form C—C and C—H* ***sigma*** *(σ) bonds.*

3.1.19 *The 6 remaining p_z orbitals overlap to form one molecular orbital with one lobe above and one lobe below the ring.*

3.1.20 *6* ***delocalised electrons*** *occupy the molecular orbital. Molecules with this feature are described as* ***aromatic*** *while other molecules are* ***aliphatic****.*

3.1.21 *Most reactions of benzene involve attack of an electrophile on the cloud of delocalised electrons, that is* ***electrophilic substitution.***

Stereoisomerism

3.1.22 *Stereoisomers have identical molecular formulae and the atoms are bonded together in the same order but the arrangement of the atoms in space is different, making them non-superimposable.*

Geometric isomerism

3.1.23 *Geometric isomerism is one type of stereoisomerism and can arise due to the lack of free rotation around a bond, frequently a carbon to carbon double bond.*

3.1.24 *Geometric isomers are labelled cis and trans according to whether the substituent groups are on the same side or on different sides of the carbon-carbon double bond.*

3.1.25 *Geometric isomers display differences in some physical properties.*

3.1.26 *Geometric isomerism can also influence chemical properties, for example cis-but-2-enedioic acid is more readily dehydrated than trans-but-2-enedioic acid.*

Optical isomerism

3.1.27 *Optical isomers (also called* ***enantiomers****) are non-superimposable mirror images of each other and are said to be chiral.*

3.1.28 *Optical isomerism can occur in substances in which four different groups are arranged around a carbon atom.*

3.1.29 *Optical isomers have identical physical and chemical properties, except when they are in a chiral environment, but they have an opposite effect on plane polarised light and are said to be optically active.*

3.1.30 *Mixtures containing equal amounts of both optical isomers are optically inactive and referred to as* ***racemic*** *mixtures.*

3.1.31 *In biological systems only one optical isomer of each organic compound is usually present.*

Permeating Aspects

Any study of organic chemistry involves the consideration and explanation of the physical and chemical properties of the various homologous series.

Physical properties such as melting and boiling points and miscibility with water are explained here in terms of the intermolecular forces involved.

Throughout the unit you will encounter and be expected to identify a variety of different types of reaction, some of which will be new to you. These will include:

addition	condensation	hydrolysis	oxidation
reduction	substitution	elimination	acid/base

The possible mechanisms of some of these reactions are discussed in detail.

All chemical reactions involve the breaking and making of bonds. The way in which bonds break has an important bearing on the direction a reaction will take and on the mechanism of that reaction. Breaking bonds is sometimes called bond fission.

In covalent bonding, electrons are shared in pairs between two atoms, e.g. in the HBr molecule:

H:Br

When the bond breaks, these electrons are redistributed between the two atoms. There are two ways in which this redistribution can happen.

Homolytic fission

In this type of bond fission, the two shared electrons separate equally, one going to each atom:

H**:**Cl → H• + Cl•

The dot• beside each atom represents the unpaired electron that the atom has retained from the shared pair in the bond. The atoms are electrically neutral because each has equal numbers of protons and electrons. However, the atoms are highly reactive because the unpaired electron has a strong tendency to pair up with another electron from another atom or molecule.

Such highly reactive atoms or groups of atoms containing unpaired electrons are called **free radicals**.

Free radicals are most likely to be formed when the bond being broken has electrons that are more or less equally shared.

Heterolytic fission

When the bond breaks, both of the shared electrons go to just one of the atoms, e.g.

H**:**Br → H^+ + **:**Br^-

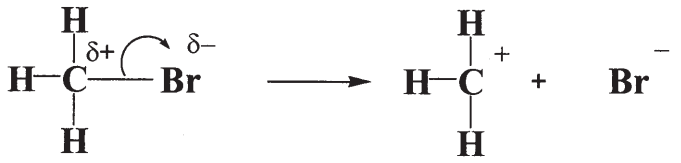
Heterolytic fission is more likely when a bond is already polar, though the ability to cope (stabilise) any charges formed can also be important.

non-polar covalent — polar covalent — ionic

$\Delta EN = 0$ — ΔEN increasing

For example, bromomethane contains a polar carbon to bromine bond and under certain conditions this can break heterolytically (Figure 1).

Figure 1



It should be noted that the CH_3^+ ion contains a positively charged carbon atom. The CH_3^+ ion is an example of a **carbocation** (also called a **carbonium** ion). Sometimes heterolytic fission can lead to the formation of ions containing a negatively charged carbon atom. These ions are called **carbanions**. Generally speaking, both these types of ions tend to be unstable and highly reactive. Consequently, they only exist as short-lived reaction intermediates.

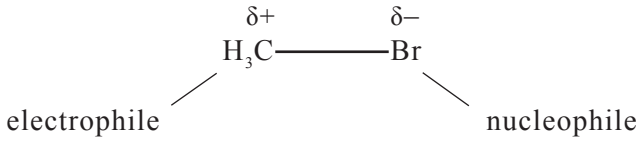
In understanding the nature of organic reactions, two other terms are extremely useful, namely **electrophiles** and **nucleophiles**.

The word 'electrophile' means literally 'electron lover' or 'electron seeker'. In other words, electrophiles are atoms or groups of atoms that are deficient in electrons and are attracted to groups that can donate electron pairs. Carbocations (carbonium ions) contain a positively charged carbon atom and so are electrophilic.

The word 'nucleophile' means literally 'nucleus lover' or 'nucleus seeker'. In other words, nucleophiles are atoms or groups of atoms that are rich in electrons and are attracted to positively charged centres. Carbanions contain a negatively charged carbon atom and so are nucleophilic.

The terms 'electrophile' and 'nucleophile' do not apply only to ions. Many organic compounds are polar. They carry partial charges, although not full positive and negative charges. These partial charges can also act as electrophilic or nucleophilic centres (Figure 2).

Figure 2



Examples of electrophiles	**Examples of nucleophiles**
carbocations, R^+	carbanions, R^-
other cations, e.g. H^+ , NO_2^+	other anions, e.g. OH^-, CN^-
electron-deficient centres	molecules with lone pairs of electrons, e.g. $:NH_3$
positively polarised centres in molecules, e.g. H in H_2O	negatively polarised centres in molecules, e.g. O in H_2O

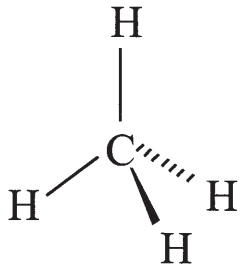
The study of the vast number of organic compounds is simplified by classification into smaller groups according to similarities and differences in the structures of their individual molecules.

Specific groupings of atoms within a molecule give those molecule particular characteristic properties. These specific groupings of atoms are known as **functional groups**. You may already have encountered some of these, e.g. hydroxyl, carbonyl, carboxyl and ester groupings. Organic compounds can be classified systematically by considering the functional groups present in the molecules.

Bonding in Hydrocarbons

Hydrocarbons are compounds containing the elements carbon and hydrogen only. This broad grouping contains a number of further sub-divisions including the familiar homologous series of alkanes, alkenes, alkynes and cycloalkanes met in previous courses.

Bonding in alkanes ***Figure 3***



Alkanes are a saturated series of hydrocarbons fitting the general formula C_nH_{2n+2}. This means that every carbon atom in any alkane molecule forms four covalent single bonds, i.e. in each carbon atom there are four bonding pairs of electrons. We can predict that these four bonding pairs will mutually repel and take up a tetrahedral arrangement, as seen in the tetrahedral methane molecule (Figure 3).

One way to consider the formation of a covalent bond is as the overlap of a half-filled atomic orbital on one atom with a half-filled atomic orbital on another atom. The two electrons in the bond are now attracted by two nuclei. Thus the overlap of the two atomic orbitals gives rise to a molecular orbital in which the two bonding electrons, now paired up, move under the influence of both nuclei.

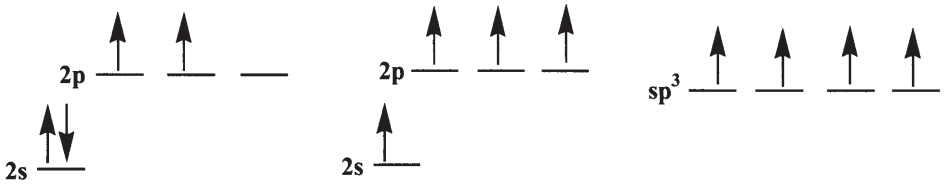
The electron arrangement of an isolated carbon atom in the ground state is $1s^2\ 2s^2\ 2p^2$. The two electrons in the 2p sublevel will occupy individually two of the three p orbitals according to Hund's rule (see Unit 1).

So, there are, therefore, only two unpaired electrons and one might expect that only two covalent bonds would be formed. Clearly, this is not the case. Methane, the simplest alkane, has the formula CH_4 and obviously contains carbon atoms forming four bonds.

This can be explained by the concept of hybrid orbitals. These are considered to result from the 'mixing' of atomic orbitals to generate a new set of orbitals. There is a solid mathematical basis for doing this based on the Schrödinger wave equations. Thankfully, you do not need to know anything about the complex calculations involved, only about the end result! The calculations predict the shapes of the hybrid orbitals as sketched in Figure 3.

In each carbon atom in methane and other alkanes, the 2s orbital and all three 2p orbitals mix to generate four equivalent hybrid orbitals. The 2s and 2p sublevels are close in energy. One of the 2s electrons has to be promoted to the third 2p orbital. This results in a carbon atom containing four singly occupied orbitals, which can be mixed to produce four hybrid orbitals of equal energy (Figure 4).

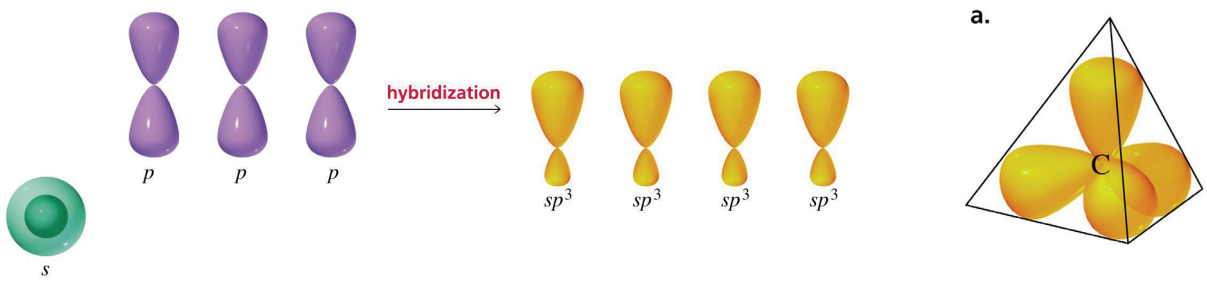
Figure 4: *sp^3 hybridisation*



carbon atom before promotion | carbon atom after promotion | carbon atom after hybridisation

The energy required to promote the electron is more than compensated for when the hybrid orbitals form bonds with other atoms since there is much more effective overlap using the hybrid orbitals. The hybrid orbitals are much more directional in shape than the unhybridised orbitals and consequently provide better overlap when forming bonds with other atoms. Since there are four hybrid orbitals, four bonds can now be formed.

***Figure 5**: Orbital shapes*



One 2 orbital and 3 p orbitals four sp^3 hybrid orbitals

For simplicity, the small lobe of the sp^3 hybrid orbital is omitted from subsequent diagrams. The four hybrid orbitals are arranged tetrahedrally around the nucleus, giving exactly the overall geometry that minimises electron repulsion. Since these hybrid orbitals are formed from one s orbital and three p orbitals, this process is known as sp^3 hybridisation and the hybrid orbitals are called sp^3 orbitals.

The formation of methane can be illustrated as shown in Figure 6. A similar process can be used to explain the formation of an ethane molecule (Figure 7).

***Figure 6**: Molecular orbitals in methane*

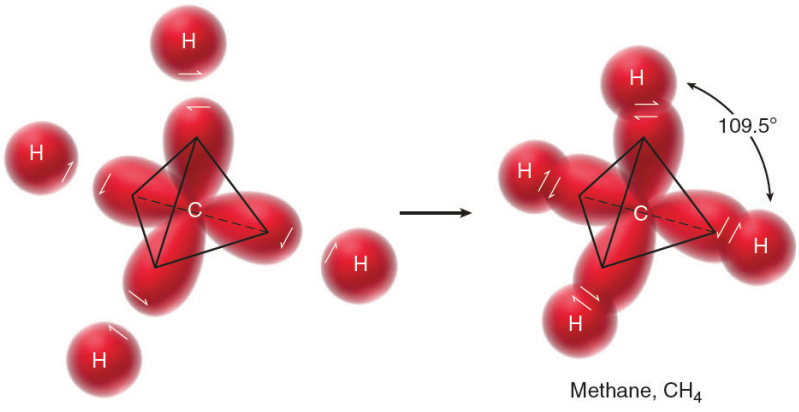
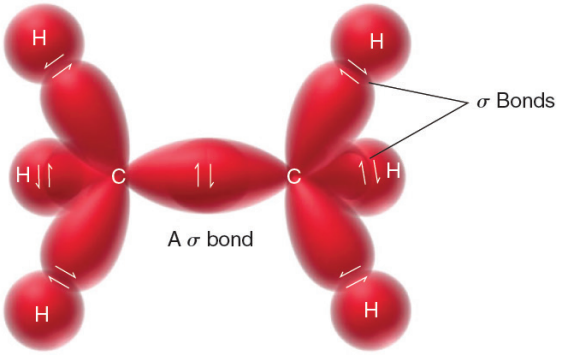


***Figure 7**: Molecular orbitals in ethane*



All the covalent bonds in these molecules – indeed for all alkanes – are formed by end-on overlap of atomic orbitals lying along the axis of the covalent bond. Such covalent bonds are known as **sigma** (σ) bonds.

Reactions of alkanes (*In future will be covered by end of Higher)

The alkanes are relatively unreactive compared with other organic compounds. They do not react with acids or alkalis. Liquid paraffin, a mixture of alkanes, is used as an inert liquid in the storage of sodium and other alkali metals to prevent their reaction with air and moisture. As you will know from Higher, alkanes are widely used as fuels because of their ease of combustion. The only other reaction of importance at ordinary temperatures is their reaction with chlorine or bromine.

Reaction with bromine is relatively slow and only takes place in the presence of sunlight. Reactions with chlorine are generally faster but still require light. In both cases, the corresponding hydrogen halide is formed. These observations are best explained by a reaction mechanism involving a **free radical chain reaction**. Remember that a free radical is an atom or molecule containing an unpaired electron.

Consider the reaction of an alkane (R–H) with bromine. R represents the rest of the molecule, e.g. in methane, $H_3C–H$, R is a methyl group.

The first stage in the reaction is the initiation step. Light (hν) supplies the correct amount of energy to break the Br–Br bond.

> ***Question***
>
> Calculate the wavelength of light required to break the Br—Br bond using the bond enthalpy of the Br—Br bond (Data Booklet).

Breakage of the bond forms two bromine atoms each with an unpaired electron:

initiation Br_2 $Br\bullet + \bullet Br$

unpaired electrons

The Br–Br bond has split so that one electron of the pair has gone to each atom. This type of bond breaking is known as **homolytic fission** .

The second stage in the reaction is the propagation step. Since free radicals are very reactive intermediates, there is a strong tendency for unpaired electrons to pair up. A bromine atom can do this by removing a hydrogen atom from an alkane molecule to form a hydrogen bromide molecule:

propagation 1 $R–H + \bullet Br \rightarrow R\bullet + H–Br$

This also produces another free radical, R•, which in turn reacts with a bromine molecule to form the bromoalkane and another bromine atom:

propagation 2 $R\bullet + Br–Br \rightarrow R–Br + \bullet Br$

This bromine atom can attack another alkane molecule and in doing this the chain reaction is propagated. These two propagation steps will continue in turn until one of the reactants is used up.

The chain will be terminated whenever any remaining free radicals meet and combine:

termination	R•	+	R•	R–R
	Br•	+	Br•	Br–Br
	R•	+	Br•	R–Br

This mechanism is consistent with the observed facts. Light is necessary to start the reaction but once started the reaction will continue in darkness. The products of the reaction are the bromoalkane and hydrogen bromide.

However, depending on the relative proportions of the reactants, multiple substitution of the alkane can take place and in order to ensure that monosubstitution predominates, a large excess of the alkane is used. The boiling point of the bromoalkane is significantly higher than that of the alkane and so the excess alkane can be easily removed by distillation. However, the reaction is not specific and any hydrogen atom in the alkane may be substituted. The more complex the alkane, the more complex will be the mixture that is obtained.

A useful memory aid for the reaction of bromine with alkanes is to remember the 'S's:

Saturated hydrocarbon (**S**ingle bonds)

Slow, **S**ubstitution reaction, which takes place in **S**unlight

Bonding in alkenes

The alkenes are an unsaturated homologous series of hydrocarbons fitting the general formula, C_nH_{2n}. Each alkene molecule contains one carbon-to-carbon double bond.

In trying to describe the formation of a double bond between two carbon atoms a variety of models can be used. For any model to be acceptable, it must be able to explain the observed facts and measurements. For example, spectroscopic measurements confirm that the bond angles in methane and ethane are 109.5°. Our sp^3 hybridisation bonding model for methane and ethane is consistent with this observation.

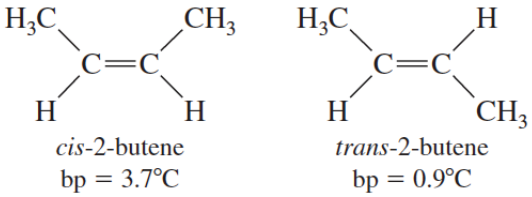
What are the key facts about the ethene molecule?

- Electron diffraction shows that the ethene molecule is planar, with bond angles of 120°.
- The carbon-to-carbon double bond is shorter than the carbon-to-carbon single bond.
- Bond enthalpies (Table 1) show that the carbon-to-carbon double bond is stronger than the carbon-to-carbon single bond but not twice as strong.

Table 1

	C—C	**C = C**	**C ≡ C**
Bond enthalpy (kJ mol^{-1})	337	607	828
Bond length (nm)	0.154	0.134	0.121

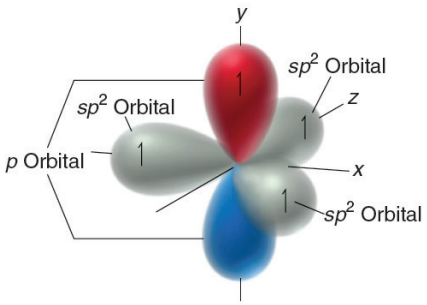
- There is restricted rotation around the carbon-to-carbon double bond. For example, but-2-ene has the structural formula $CH_3CH=CHCH_3$. However, it exists as two different geometric isomers (see later Section on Stereoisomerism):



In the *trans*-isomer, the hydrogen atoms are on opposite sides of the double bond. In the *cis*-isomer, the hydrogen atoms are on the same side. Clearly rotation about the carbon-to-carbon double bond is difficult, unlike the situation with a single bond where there is comparatively free rotation. For example,1,2-dibromoethane does not exhibit similar isomerism.

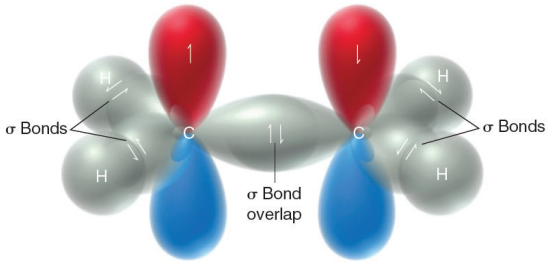
Once again, a bonding model involving hybridisation can explain these facts. In this case, sp^2 hybridisation takes place. Each carbon atom uses the 2s orbital and only two of the 2p orbitals. Promotion and mixing as before give **three** identical sp^2 hybrid orbitals (Figure 8).

***Figure 8**: sp^2 hybridisation*



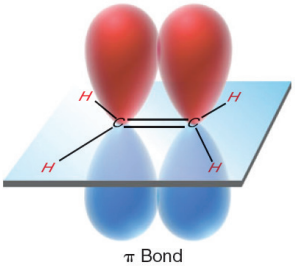
The three hybrid orbitals lie at 120° to each other in a plane perpendicular to the unhybridised 2p orbital. In ethene (Figure 9), the hybrid orbitals are used to form sigma (σ) bonds to hydrogen atoms and also to link the two carbon atoms (as shown).

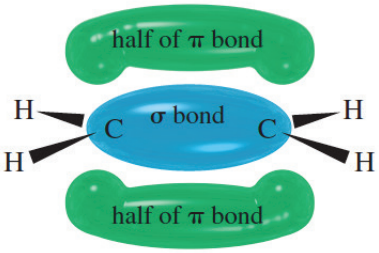
Figure 9



Remember that sigma bonds are formed by end-on overlap of atomic orbitals lying along the axis of the bond. In ethene, each carbon atom also has an unhybridised 2p orbital perpendicular to the plane of the molecule. These orbitals are parallel to each other and close enough to each other to overlap above and below the plane of the sp^2 bonds. This overlap produces a new molecular orbital between the two carbon atoms, with lobes above and below the molecular plane (Figure 10).

***Figure 10**: π bond in ethene*





Such a bond formed by sideways overlap of p orbitals is known as a **pi** (π) bond. This extra bond pulls the carbon atoms closer together, shortening the bond length. Sideways overlap is less effective than end-on overlap, with the result that π bonds are not as strong as σ bonds.

Thus, the carbon-to-carbon double bond is stronger than the carbon-to-carbon single bond but not twice as strong. π overlap between the two p orbitals is most effective when the p orbitals are parallel. If one end of the molecule is twisted relative to the other, then the amount of overlap is reduced and eventually the π bond will be broken.

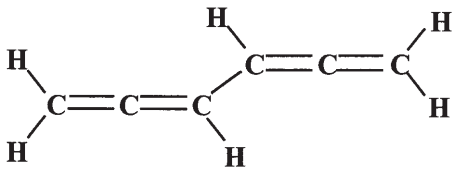
This will require a lot of energy and so our model also explains the restricted rotation about the carbon-to-carbon double bond.

Bonding in Benzene & Other Aromatics

The term '**aromatic**' was first used to describe a group of natural oils, many of which were pleasant smelling. As more and more similar compounds were discovered, it became apparent that many had an unpleasant smell. Indeed, some are toxic and smelling the vapours can be very dangerous.

The common link between these compounds was not a similarity in their smells but a similarity in their structures. The term 'aromatic' is still retained to indicate a particular structure and characteristic chemical behaviour. The systematic name for the family of aromatic hydrocarbons is the '**arenes**'.

The simplest and most important aromatic compound is benzene, which was first isolated from whale oil in 1825 by Michael Faraday. The molecular formula of benzene was first established as C_6H_6 in 1834 but its structure remained a source of controversy for many years.

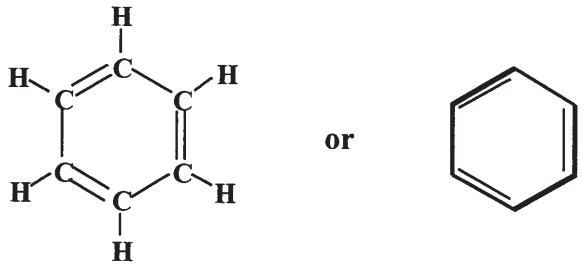


Bonding and structure of benzene ***Figure 11***

A variety of highly unsaturated structures were initially suggested for benezene, including the hexatetraene shown in Figure 11.

Monosubstitution by chlorine can occur either on the end carbon atoms or on the middle carbon atoms, giving rise to two possible isomers. However, chlorobenzene, C_6H_5Cl, does not exhibit isomerism. The problem was partly solved by Kekulé in 1865 when he proposed a ring structure with alternating single and double bonds (Figure 12).

Figure 12



In this structure all the hydrogen atoms are identical and so there can be only one form of chlorobenzene. However, Kekulé's structure was unable to explain other subsequent observations and measurements:

- X-ray diffraction shows that the carbon-to-carbon bond lengths are all the same (139 pm), shorter than the carbon-to-carbon single bond length (154 pm) but longer than the carbon-to-carbon double bond length (133 pm). In sharp contrast, Kekulé's structure predicts alternating short and long bonds.

- Benzene is more thermodynamically stable than Kekulé's structure suggests. The standard enthalpy of formation of gaseous benzene is +82 kJ mol^{-1}, based on measured enthalpies of combustion:

- $6C(s) + 3H_2(g)$ $C_6H_6(g)$

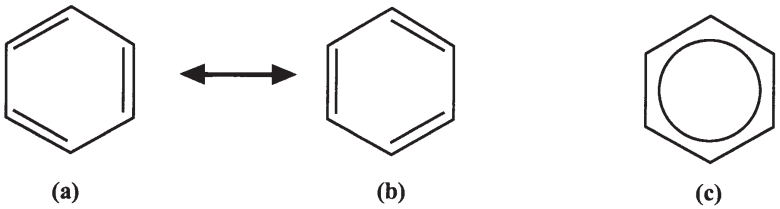
- Benzene is resistant to the addition of bromine. If the ring contained three carbon-to-carbon double bonds, bromine would be expected to add easily, as is the case with alkenes.

Question

Using the bond enthalpy information in the Data Booklet, calculate the theoretical enthalpy of formation of gaseous benzene using the Kekulé structure. Compare your answer to the measured value.

One proposal to explain these observations was to describe the structure of benzene in terms of two different 'resonance structures' (Figure 13).

Figure 13



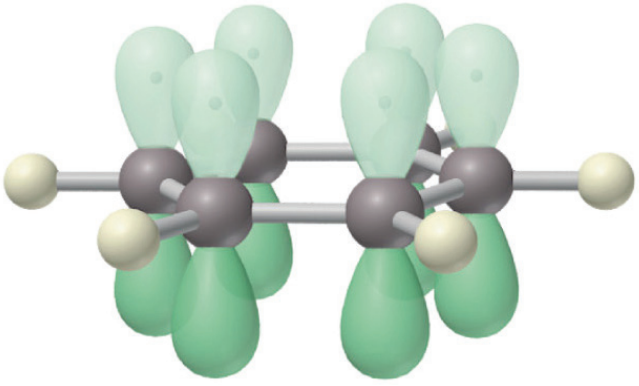
Though we now know that structures (a) and (b) are 'incorrect' they can still be useful but the reality is closer to the structure shown in (c) in Figure 13.

A more satisfactory explanation of the structure involves sp^2 hybridisation.

In ethene, a planar σ framework with 120° bond angles was proposed, with the remaining two electrons shared between the two carbon atoms as a π-bonding pair.

For benzene a similar σ framework can be envisaged, as in Figure 14. The hydrogen atoms lie in the plane of the ring, pointing away from the ring.

Figure 14



The six carbon atoms form a regular planar hexagonal ring. Each p orbital contains one electron. Sideways overlap is possible with each adjacent p orbital. The result is that the six electrons become delocalised and occupy two continuous doughnut-shaped electron clouds, one above and one below the planar σ framework (Figure 15).

Figure 15

The delocalisation of the electrons helps to bond the atoms more tightly together. The result is a completely symmetrical molecule, with considerable stability. This type of delocalised structure is the common feature shared by aromatic hydrocarbons.

Indeed, the term 'aromatic' can be redefined to describe any system that contains a ring of atoms stabilised by delocalised π electrons. Compounds that contain molecules with straight- or branched-chain carbon skeletons are described as ***aliphatic***.

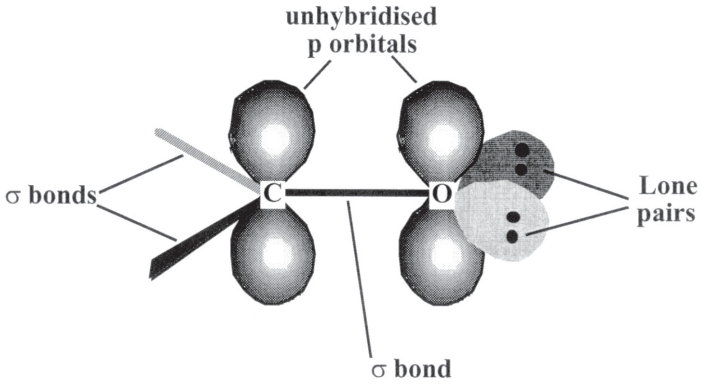
Bonding in Carbonyls

The chemistry of these families of organic compounds is an extremely important segment of organic chemistry and was first considered at Higher.

The structural feature that they all have in common is the carbonyl group, C=O. We can envisage the formation of the carbon-to-oxygen double bond in a similar manner to that of the carbon-to-carbon double bond in alkenes.

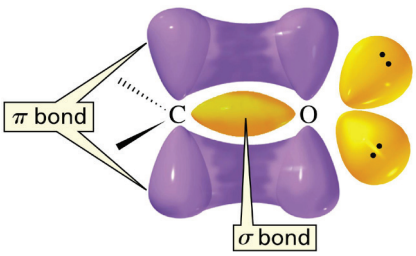
Thus, both the carbon atom and the oxygen atom are sp^2 hybridised allowing the formation of a σ bond by sharing a pair of electrons between the carbon and oxygen atoms (Figure 16).

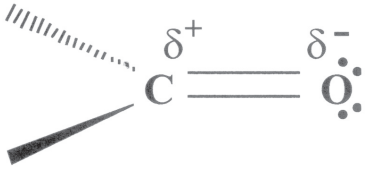
Figure 16



Sideways overlap of the unhybridised p orbitals forms a π bond (Figure 17).

Figure 17





This model fits the observed facts. The bond angles are 120° and the group is planar. Unlike the carbon-to-carbon double bond, the carbonyl group is significantly polar because of the strong attraction of the oxygen atom for the bonded pairs of electrons. The polar nature of the bond is confirmed by the high dipole moment of the carbonyl group.

It follows that in all three families of compounds the physical properties and chemistry are governed by the polar nature of the carbonyl group.

In addition, the tendency of the carboxylic group to ionize (Figure 18) is down to extra stability achieved through the extension of the molecular orbitals.

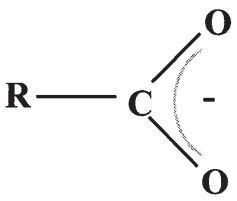
Figure 18

The presence in the carboxyl group of a carbonyl group adjacent to the OH group is responsible for this increased acidity. The carboxylate ion formed on dissociation is shown in Figure 13 as containing a double bond to one oxygen atom and a single bond to the other.

In fact, X-ray diffraction studies show that the bond lengths of both carbon to oxygen bonds in the carboxylate ion are identical, suggesting that the two bonds are identical.

This can be explained by further sideways overlapping of p orbitals, the delocalisation of the electrons over the whole carboxylate group (Figure 19).

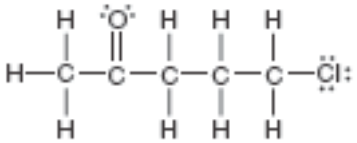
Figure 19



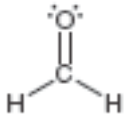
The spreading of the negative charge stabilises the carboxylate ion and means that it is less likely to recombine with a hydrogen ion.

Questions

1. The regions of δ+ in a compound are the regions most likely to be attacked by a nucleophile such as hydroxide (HO^-). In the compound below, identify the two carbon atoms that are most likely to be attacked by a hydroxide ion:



2. Consider the structure of formaldehyde:



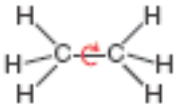
formaldehyde (methanal)

a) Identify the type of bonds that form the C=O double bond.

b) Identify the hybrid orbitals that form each C—H bond.

c) What type of atomic orbitals do the lone pairs occupy?

3. Sigma bonds experience free rotation at room temperature:

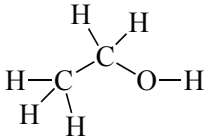


In contrast, π bonds do not experience free rotation. Explain.

Different Types of Formulae

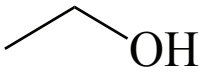
By now you should be familiar with:

- **Molecular formula** is the actual number of atoms of each element in a molecule e.g. $\mathbf{C_2H_6O}$ for ethanol
- **Empirical formula** is the simplest whole number ratio of the atoms of each element in a molecule e.g. $\mathbf{CH_2}$ for ethene (from molecular formula $C_2H_4 \div 2$)
- **General formula** is the simplest algebraic formula for a member of a homologous series e.g. $\mathbf{C_nH_{2n+2}}$ for alkanes
- **Structural formula** shows the relative positioning of atoms and the bonds between them e.g. for ethanol:



In addition you should become familiar with:

Skeletal formula shows just the carbon skeleton and functional groups e.g. for ethanol



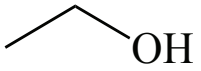
Skeletal formulae show carbon-carbon bonds and functional groups only. Neither the carbon atoms, nor any hydrogen atoms attached to the carbon atoms, are shown.

There is a carbon atom at the end of a line and the presence of other carbon atoms are implied by a 'kink' in the backbone.

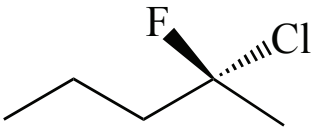
Alkane **e.g. hexane**

Alkene **e.g. hex-3-ene**

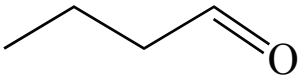
Alcohol **e.g. ethanol**



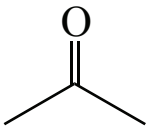
Halogenoalkane **e.g. 2-chloro-2-fluoropentane**



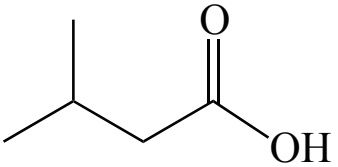
Aldehyde **e.g. butanal**



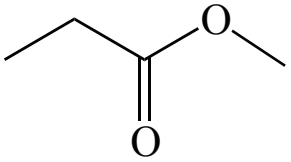
Ketone **e.g. propanone**



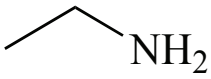
Carboxylic acid **e.g. 3-methylbutanoic acid**



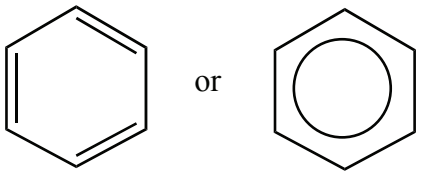
Ester **e.g. methyl propanoate**



Amine **e.g. ethylamine**



Benzene



Questions

1. Draw ***skeletal formulae*** for each of the following

a. propane, $CH_3CH_2CH_3$

b. methoxymethane, CH_3OCH_3

c. propyne, $HC{\equiv}CCH_3$

d. methylcyclopropane, $(CH_2)_2CHCH_3$

e. ethanal, CH_3CHO

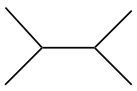
f. tetrafluoroethene, $F_2C{=}CF_2$

g. propadiene, $CH_2{=}C{=}CH_2$

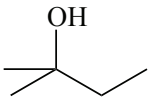
h. benzenamine, $C_6H_5NH_2$

2. Draw ***structural formulae*** for and ***name*** each of the following

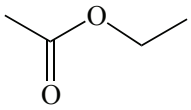
a.



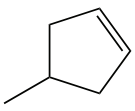
b.



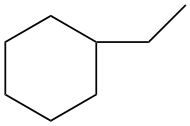
c.



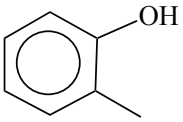
d.



e.



f.

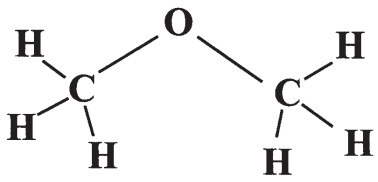


Stereoisomerism

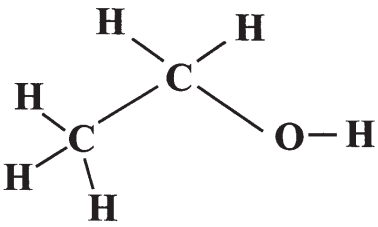
Isomerism is an interesting and important feature of organic chemistry. It occurs whenever there is more than one way to organise a given number of atoms into a molecule. Isomers have been defined as 'compounds with the same molecular formula but different structural formulae'.

In **structural isomerism**, the molecules differ in terms of the order in which the atoms are joined together. For example, there are two possible isomers with the molecular formula, C_2H_6O (Figure 20).

Figure 20



methoxymethane



ethanol

In methoxymethane, the oxygen atom lies between the two carbon atoms whereas in ethanol the two carbon atoms are bonded together with the oxygen at the end. Clearly, the two substances belong to different homologous series and will have very different chemical and physical properties.

In **stereoisomerism**, the molecules differ only in the orientation of the atoms in space. They have identical molecular formulae and the atoms are bonded together in the same order. However, because the arrangement of the atoms in space is different, the molecules are non-superimposable.

This means that no matter how hard you try it is impossible to superimpose the image of one molecule on top of the other. We will consider the following types of stereoisomers: geometric and optical. Students are strongly encouraged to use molecular models to show exact molecular shapes in all aspects of isomerism.

Question

1. Propane was reacted with chlorine. The following products were obtained:

- hydrogen chloride
- two compounds of formula C_3H_7Cl
- four compounds of formula $C_3H_6Cl_2$ (labelled A, B, C and D).

a) What type of reaction has taken place and what type of bond fission occurred?

b) Draw full structural formulae for all the organic compounds.

Geometric isomerism

Geometric isomerism is one type of stereoisomerism and generally arises because of the lack of free rotation around a bond, especially a carbon-to-carbon double bond. As was seen earlier (see page 14), rotation around the double bond is restricted because it would involve breaking the π bond.

Consequently, if both carbon atoms of the double bond each carry a single substituent, then two isomers will exist, one with the substituents on the same side of the double bond, the other with the substituents on the opposite sides, e.g. but-2-ene (Figure 21).

Figure 21

a) *trans*-but-2-ene **b) *cis*-but-2-ene**

If the substituents are on opposite sides, the isomer is called the *trans*-isomer whereas if the substituents are on the same side it is called the *cis*-isomer. Structure (a) in Figure 21 is the *trans*-isomer since both methyl groups are on opposite sides (as are the two hydrogen atoms) whilst structure (b) is the *cis*-isomer since the methyl groups are on the same side.

This situation can also occur with di-substituted cycloalkanes (Figure 22).

Figure 22

a) *trans*-1,2-dibromocyclopropane ***b)*** *cis*-1,2-dibromocyclopropane

Geometric isomers generally display differences in physical properties, as shown in Table 2.

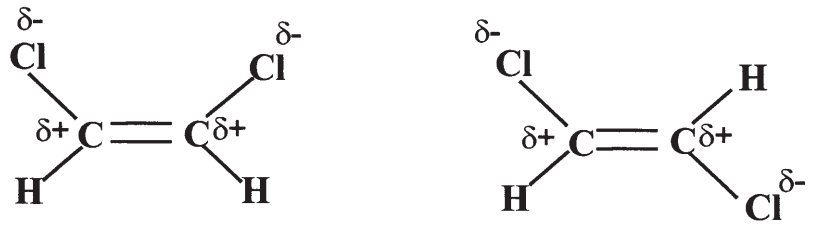
Table 2

Isomer	***Melting point °C***	***Boiling point °C***
cis-But-2-ene	–139	+4
trans-But-2-ene	–106	+1
cis-Dichloroethene	–80	+60
trans-Dichloroethene	–50	+48

The differences in the melting points can be explained in terms of the differences in the shapes of the molecules. It appears likely that molecules of the *trans*-isomers are able to pack more closely together in the solid state than the *cis*-isomers. This close packing increases the van der Waals' forces between the molecules and hence increases the melting point. On the other hand, differences in boiling point seem to be due to slight differences in polarity between the *cis*- and *trans*-isomers.

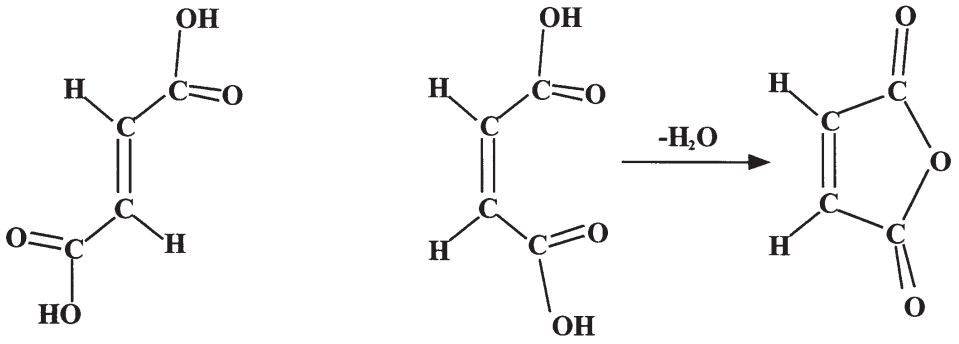
In both geometric isomers of 1,2-dichloroethene the C–Cl bonds are polar (Figure 23). In the *cis*-isomer, both bonds lie on the same side of the double bond and so the molecule itself will be polar. However, because of the symmetry of the *trans*-isomer, the polarities of the bonds cancel each other out and so the molecule itself is non-polar. As a result of these extra polar–polar attractions between the molecules of the *cis*-isomer, the *cis*-isomer has a higher boiling point than the *trans*-isomer.

Figure 23



In certain cases, geometric isomers can also display different chemical properties. An example is the relative ease of dehydration of the two isomers of but-2-enedicarboxylic acid (Figure 24).

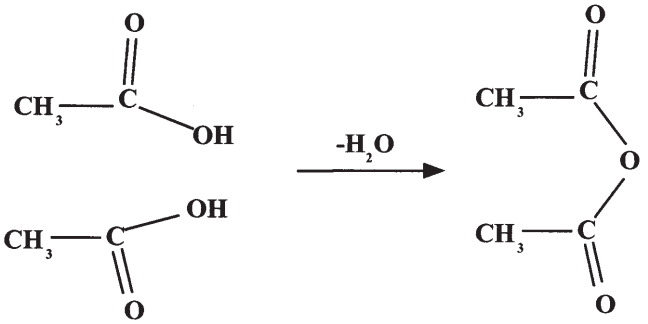
Figure 24



a) ***b)***

The condensation, with elimination of water, of two carboxyl groups produces an acid anhydride, e.g. two molecules of ethanoic acid can condense to give ethanoic anhydride (Figure 25).

Figure 25



When the *cis*-isomer of but-2-enedicarboxylic acid, which has two carboxyl groups on the same side of the double bond, is heated an internal condensation reaction takes place to produce but-2-enedioic anhydride (see Figure 24b).

This is clearly not possible for the *trans*-isomer (Figure 24a) since the carboxyl groups are on opposite sides and there is restricted rotation about the carbon-to-carbon double bond.

Fats and edible oils are naturally occurring esters of glycerol (propane-1,2,3-triol) and long-chain carboxylic acids called fatty acids. Edible oils are simply liquid fats. The fatty acids are almost exclusively straight-chain molecules, with an even number of carbon atoms usually ranging from about 10 to 20.

The chains may be saturated, monounsaturated or polyunsaturated (more than one carbon-to-carbon double bond per molecule). Animal fats tend to have a higher proportion of saturated fatty acids whereas vegetable oils have a higher proportion of unsaturated fatty acids.

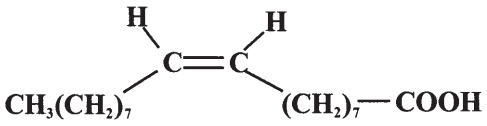
Recent medical research has linked a diet that is high in saturated fats with high levels of cholesterol in the blood. This leads to a build-up of fatty deposits in arteries and an increase in the incidence of heart disease.

Unsaturated fats have not been similarly implicated and so health authorities have been advising people to cut down on the total amount of fat in their diet and also to replace sources of saturated fat with unsaturated fats wherever possible.

Most of the important unsaturated fatty acids have a *cis*-arrangement around their carbon-to-carbon double bonds (Figure 26).

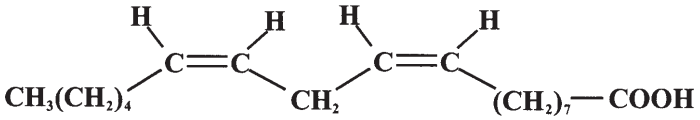
Figure 26

oleic acid



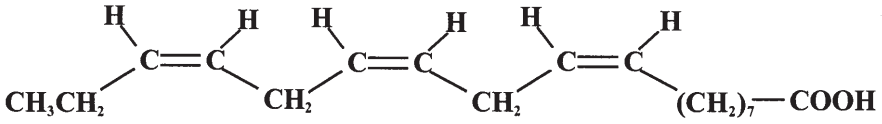
(octadec-*cis*-9-enoic acid)

linoleic acid



(octadec-*cis*-9,*cis*-12-dienoic acid)

linolenic acid



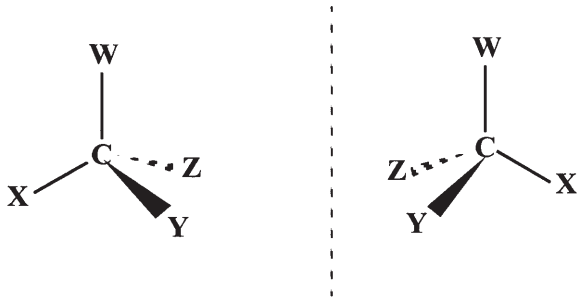
(octadec-*cis*-9,*cis*-12,*cis*-15-trienoic acid)

A few *trans*-fatty acids are found naturally, mainly in meat products and dairy foods. Current scientific evidence suggests that they behave in a similar way to saturated fatty acids in raising blood cholesterol levels.

Optical isomerism

This type of stereoisomerism arises whenever a molecule contains a tetrahedral carbon atom that has four different groups attached to it (Figure 27).

Figure 27



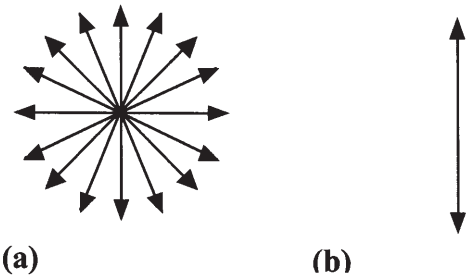
There are two possible arrangements for such a molecule, as shown in Figure 27. These differ only in that one is a mirror image of the other. Such isomers are known as ***enantiomers*** (from the Greek *enantio* meaning 'opposite'). It is impossible to exactly superimpose the structure of one enantiomer on top of the other.

(You are again encouraged to use molecular models to show this). The two molecules are said to be ***asymmetric***, i.e. they have no centre of symmetry, plane of symmetry or axis of symmetry. The molecules are described as ***chiral***. The relationship between the two molecules is a bit like the relationship between your two hands, which are also mirror images and cannot be superimposed on each other. A right-handed glove does not fit a left hand and is said to be chiral (from the Greek word for hand).

Unlike geometric isomers, ***optical isomers*** (enantiomers) have identical physical properties except that they have an opposite effect on plane polarised light. For this reason, they are said to be optically active. They also have identical chemical properties except when the reactions are carried out in a chiral (asymmetric) environment.

Light is a form of electromagnetic radiation that is most simply understood as a wave phenomenon. Light travels as a transverse wave, which means that the magnetic and electrical fields oscillate at right angles to the direction of travel of the light. A normal ray of light consists of waves vibrating in many directions at right angles to the direction of travel (see Figure 28a).

Figure 28



Certain substances only allow the transmission of light vibrating in a single plane. Passing light through such a substance produces plane polarised light (see Figure 28b). 'Polaroid' sunglasses make use of such substances to reduce glare and reflections off water.

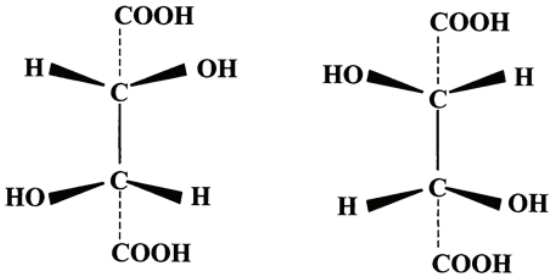
Substances that are able to rotate the plane of polarised light are said to be optically active. This phenomenon was discovered as early as 1815. In 1848, Louis Pasteur was working with an optically inactive salt of tartaric acid when he noticed that there were two different kinds of crystal which were mirror images of each other. He painstakingly separated the two crystal forms using a hand lens and tweezers into two piles.

He then discovered that solutions of each type were optically active and indeed that one kind rotated the plane of the polarised light in a clockwise direction while a solution of the other rotated the plane by exactly the same amount in the opposite direction.

Pasteur proposed that this happened because the molecules themselves must be mirror images. It was a further hundred years before the exact configurations of the two optically active isomers of tartaric acid were finally confirmed (Figure 29).

It should be noted that tartaric acid molecules contain two asymmetric carbon atoms (chiral centres).

Figure 29

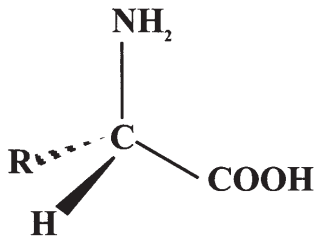


A mixture containing equal amounts of the two optical isomers is known as a ***racemic mixture*** and is optically inactive. The salt of tartaric acid with which Pasteur was working was a racemic mixture, which explains why it was optically inactive.

Chirality is extremely important in biological systems. Enzymes are complex proteins that are condensation polymers built up from monomers known as 2-amino acids or α-amino acids (general formula NH_2–CH(R)–COOH).

Figure 30

From Figure 30 it is clear that the 2-amino acid molecule is chiral and so there are two optical isomers for every amino acid found in proteins, except for glycine (2-aminoethanoic acid) where R = H. Only the optical isomer shown in Figure 30 occurs naturally in higher order living organisms such as humans.



Since the monomer units are chiral, it follows that the enzymes themselves will be chiral. If the substrate molecule on which a particular enzyme operates is chiral, then only one of the optical isomers of the substrate will fit the enzyme's active site. Consequently, the other isomer will not be biologically active.

In general, if a naturally occurring molecule can exhibit optical isomerism, only one of the optical isomers is usually present in the biological system. In this context, it is worth speculating that there is a good chance that somewhere in the universe a world exists that is entirely of the opposite handedness. If one met intelligent beings from such a world, we might be able to communicate and share ideas but we certainly could not share their food!

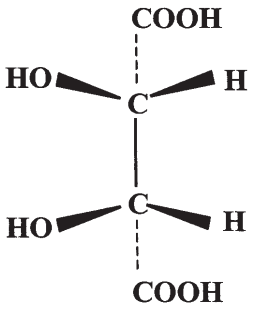
Questions

1. ***a)*** Draw structures for all possible isomers (structural and geometric) with molecular formula, C_4H_8.

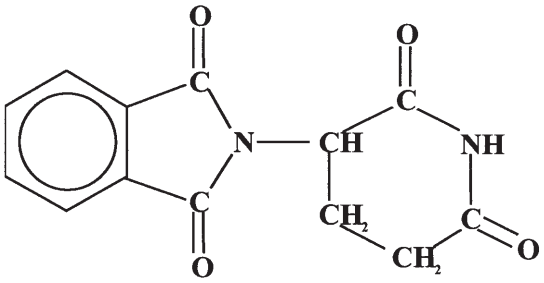
b) If that was too easy, try to draw structures for the 12 isomers with formula C_5H_{10}.

2. Draw the full structural formula for the first alkane to show optical isomerism and name the compound.

3. Would you expect the isomer of tartaric acid shown below to be optically active? Explain your answer.

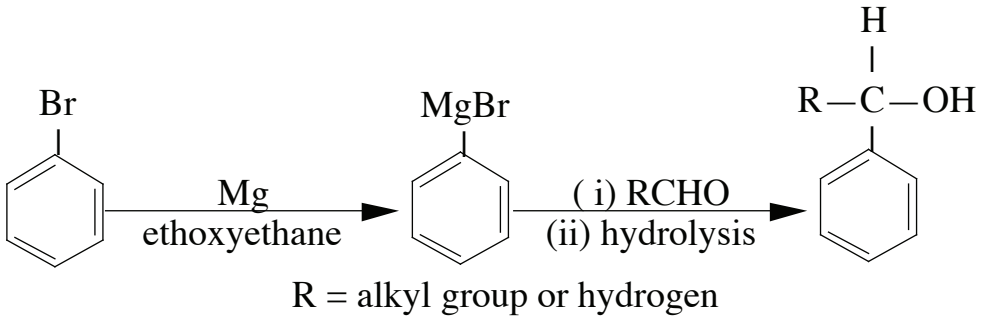


4. Thalidomide is a notorious drug. In the 1960s it was prescribed to pregnant women to treat morning sickness. There are two optical isomers. One of the isomers provided an effective treatment for the morning sickness but unfortunately the other caused serious malformation of the foetus.



From the structure above, explain why thalidomide exhibits optical isomerism.

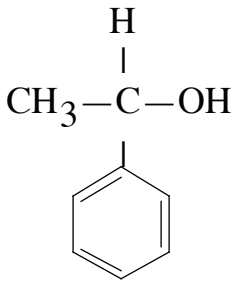
Q1



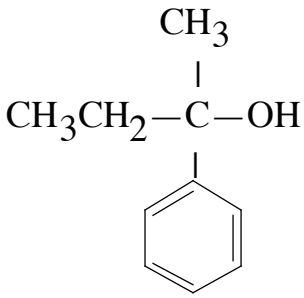
R = alkyl group or hydrogen

Using bromobenzene above and treating with propanone at (i), subsequent hydrolysis would result in the formation of

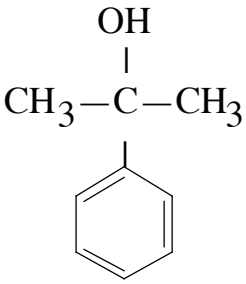
A



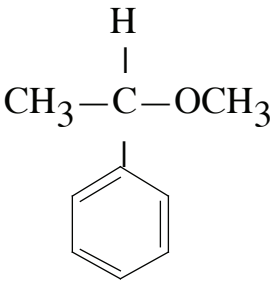
B



C



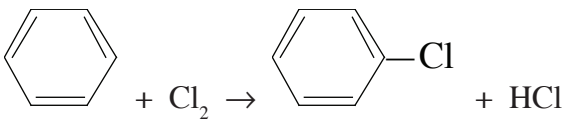
D



Q2 Which of the following does ***not*** involve a nucleophilic substitution of the organic compound?

A $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$

B



C $C_2H_5CH_2Br + CN^- \rightarrow C_2H_5CH_2CN + Br^-$

D $CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$

Q3 Which of the following can behave as an electrophile?

A $C_2H_5NH_2$

B HS^-

C NH_3

D NO_2^+

Q4 In each of the following compounds, the bonding shown is between carbon and one other element. In which compound is the bond polarised such that the carbon has a partial negative charge?

A $H_3C—Br$

B $CH_3CH=O$

C $H_3Si—CH_3$

D $CH_3C\equiv N$

Q5

$$OH^- + CO_2 \rightarrow HCO_3^-$$

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br^+ + Br^-$$

In the above two reactions, which two substances are acting as electrophiles?

A OH^- and Br_2

B OH^- and C_2H_4

C CO_2 and Br_2

D CO_2 and C_2H_4

Q6

$$C_2H_5Br + C_2H_5O^-Na^+ \rightarrow C_2H_5OC_2H_5 + Na^+Br^-$$

This reaction is an example of

A a condensation reaction to form an ether

B a condensation reaction to form an ester

C a nucleophilic substitution to form an ether

D an electrophilic substitution to form an ether

Q7 The reaction scheme shown below is an example of a chain reaction.

①			Br_2	→	2Br*		***initiation step***
②	C_2H_6	+	T	→	C_2H_5*	+ U	
③	V	+	Br_2	→	C_2H_5Br	+ W	
④	Br*	+	Br*	→	X		
⑤	C_2H_5*	+	C_2H_5*	→	Y		
⑥	C_2H_5*	+	Z	→	C_2H_5Br		

a) Write down the species represented by the letters T to Z in the reaction scheme. **3**

b) In step ①, the initiation step, explain if the process is exothermic or endothermic. **1**

c) ***i)*** What name is given to the process represented by steps ② and ③? **1**

ii) What name is given to the process represented by steps ④ to ⑥? **1**

d) Why is the reaction shown referred to as a chain reaction? **1**

(7)

Q8. The electronic arrangement for carbon is $1s^2\ 2s^2\ 2p^2$.

a) Based on this information alone, how many unpaired electrons will carbon have? **1**

b) Explain why carbon is able to form four bonds. **2**

c) The C–C bond strength is 346 kJ mol^{-1} and the C=C bond strength is 602 kJ mol^{-1}. In terms of bonding types explain why the C=C bond is not twice as strong as the C–C bond. **2**

d) Draw a molecule of ethene showing all the overlapping atomic orbitals. **1**

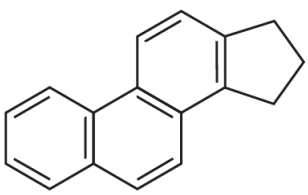
(6)

Q9. The end-on overlap of two atomic orbitals lying along the axis of a bond is known as

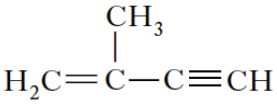
A hybridisation
B a sigma bond
C a pi bond
D a double bond. **1**

Q10. What is the molecular formula for the structure shown?

A $C_{17}H_{11}$
B $C_{17}H_{14}$
C $C_{17}H_{17}$
D $C_{17}H_{20}$



Q11. Which line in the table is correct for the following hydrocarbon?



	Number of σ bonds	Number of π bonds
A	4	3
B	8	5
C	10	2
D	10	3

1

Q12 ***a)*** The bonding in but-1-ene can be described in terms of sp^2 and sp^3 hybridisation and sigma and pi bonds.

i) What is meant by sp2 hybridisation? **1**

ii) What is the difference in the way atomic orbitals overlap to form sigma and pi bonds? **1**

b) But-2-ene forms both structural isomers and geometric isomers.

i) Draw two structural isomers of but-2-ene, one from the same homologous group and one from a different homologous group. **2**

ii) Draw the two geometric isomers of but-2-ene. **2**

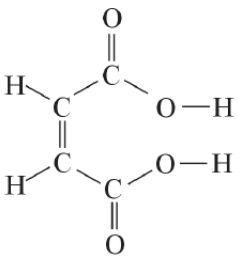
(6)

Q13. A simple test such as determining the melting point can help to distinguish between different isomers, e.g. between pentane and 2,2-dimethylpropane or between maleic acid and fumaric acid.

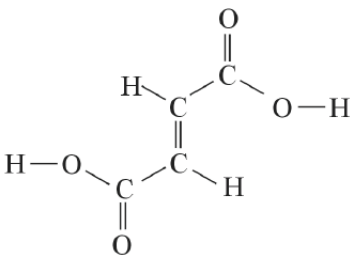
a) ***i)*** Draw the structural formulae for pentane and 2,2-dimethylpropane. **2**

ii) Use these structures to help explain which isomer will have the higher melting point. **2**

b)



maleic acid



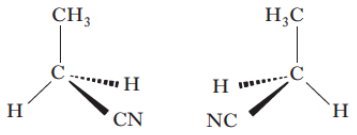
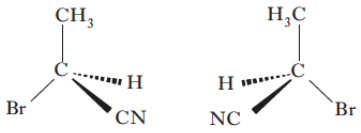
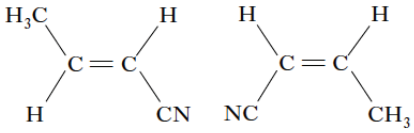
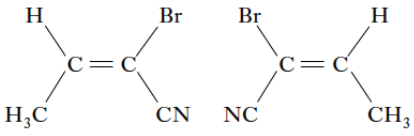
fumaric acid

i) What are the systematic names for maleic acid and fumaric acid? 2

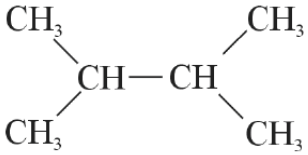
ii) By referring to their shapes explain which isomer has the higher melting point. **2**

(8)

Q14. Which line in the table shows a pair of optical isomers?

A		
B		
C		
D		

Q15. ***a)*** ***i)*** Name this molecule.



1

ii) Name the straight-chain isomer. **1**

b) Does the molecule shown have an optically active carbon?
Explain your answer. **2**

c) Draw the structural formula for a molecule that has one more carbon atom than the above molecules and also has a chiral carbon atom. **1**

(5)

Q16. Lactic acid, $CH_3CH(OH)COOH$, extracted from milk, was found to rotate the plane of polarised light, but another sample of lactic acid, which was synthesised in the laboratory, did not affect polarised light.

a) Give a systematic name for lactic acid. **1**

b) ***i)*** Draw the full structural formula for lactic acid. **1**

ii) Place an * on the carbon atom that is said to be asymmetric (the chiral centre). **1**

c) Explain why the sample synthesised in the laboratory was not optically active. **2**

(5)

Answers

Q1 C ***Q2*** B ***Q3*** D ***Q4*** C ***Q5*** C ***Q6*** C

Q7 ***a)*** T – Br*; U – HBr; V – C_2H_5*; W – Br*;
X – Br_2; Y – C_4H_{10}; Z – Br* (any 6 × ½) **3**

b) Endothermic (1)
Energy required to break bonds (1) **2**

c) ***i)*** Propagation (1)
ii) Termination (1) **2**

d) Once the Br* radical is produced, the propagation step produces more of these radicals to keep the reaction going. **1**

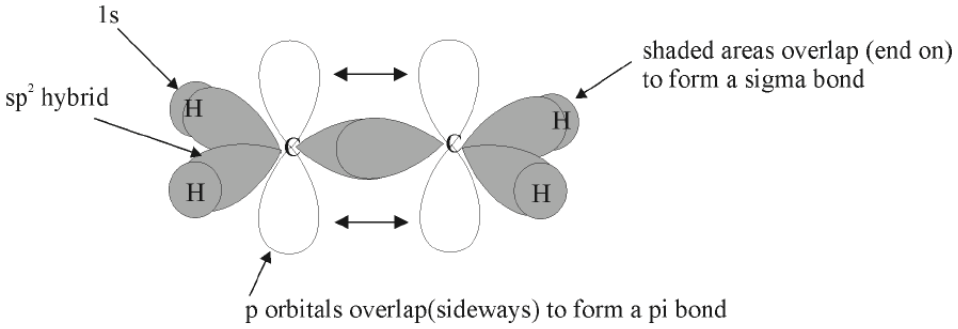
(8)

Q8. ***a)*** 2 **1**

b) The 2s and 2p orbitals combine to form four hybridised sp3 orbitals. (1)
Each occupied by one electron. (1) **2**

c) The C=C bond consists of a σ bond and a π bond (1)
but the C—C is just a σ bond. (1) **2**

d)



1

(6)

Q9 B ***Q10*** B ***Q11*** D ***Q14*** B

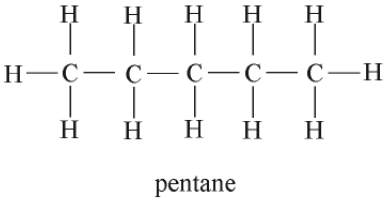
Q12 ***a)*** ***i)*** sp2 hybridisation is a mixing of one s orbital and two p orbitals,
(hybridising of one s orbital and two p orbitals) **1**

ii) Sigma bonds – end on overlap of (atomic) orbitals
Pi bonds – sideways overlap of (atomic) orbitals
2 correct diagrams **1**

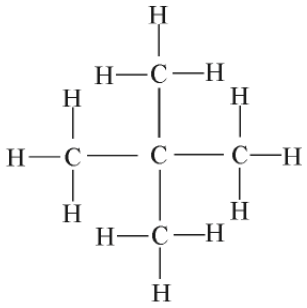
b) ***i)*** one alkene isome
one cycloalkane isomer **2**

ii) the *cis* form of but-2-ene
the *trans* form of but-2-ene **2**
(6)

Q13. ***a)*** ***i)***



pentane



2,2-dimethylpropane

2

ii) Pentane is a longer molecule and will have more van der Waals' forces between the molecules (1)
and thus will have a higher boiling point. (1)
2

b) ***i)*** Maleic acid is cis-butenedioic acid;
fumaric acid is trans-butenedioic acid. (1+1) **2**

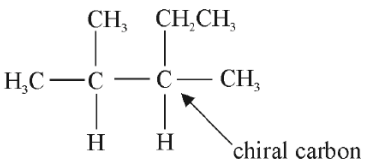
ii) The trans isomer will be able to form hydrogen bonds with neighbouring molecules but the cis isomer will form hydrogen bonds with the other acid group on the same molecule. (1)

The trans isomer will have the higher melting point. (1)
2
(8)

Q15. ***a)*** ***i)*** 2,3-dimethylbutane **1**
ii) Hexane **1**

b) No (1)
Four of the C atoms have more than one H atom attached, and two have methyl groups attached therefore none of them has four different groups attached. (1) **2**

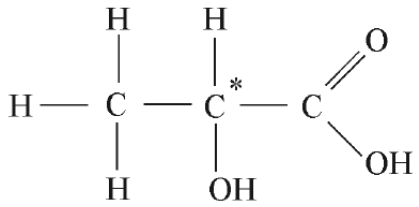
c)



1
(5)

Q16. ***a)*** 2-hydroxypropanoic acid **1**

b)



2

c) It is a racemate (racemic mixture), i.e. it consists of equal amounts of the two enantiomers. **2**

(5)