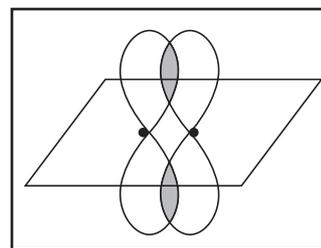# Fundamental Principles and Special Topics

One begins a study of reaction mechanisms by examining some of the basic principles. A basic understanding of these concepts helps largely in understanding of reactions and their mechanisms. Thiols undergo an oxidative coupling when treated with mild oxidizing agents to give disulphides: $2RS{-}H + H_2O_2 \longrightarrow RS{-}RS + 2H_2O$. The understanding of this reaction requires a knowledge of bond dissociation energy. The bond dissociation energy of the S—H bond of thiols (~ 80 kcal/mol) is much lower than the O—H bond of alcohols (~ 100 kcal/mol). It is this weakness of the S—H bond which allows thiols to undergo an oxidative coupling, and the alcohols do not display this reaction. On treatment with oxidizing agents, oxidation at the weaker C—H bond (~ 85 kcal/mol) takes place rather than at the strong O—H bond. Thus a knowledge of the nature and strength of bonds is essential for the chemical investigation of organic molecules. Similarly the properties of molecules are influenced by their structure.

1.1 STRUCTURE AND BONDING IN ORGANIC COMPOUNDS

A. Atomic Orbitals

The motion of the electrons around the nucleus can be described by wave equations. The solutions to these equations are atomic orbitals, which roughly delineate regions in space where there is a high probability of finding the electron. An s orbital is spherical; a p orbital looks like two touching spheres, or a "spherical figure eight" (Scheme 1.1). The sign of the orbital can be positive, negative, or zero (node). These signs do not represent positive or negative charges, since both lobes of an electron cloud must be negatively charged. They refer to the signs of


1s orbital $2p_x$ orbital $2p_x$, $2p_y$, and $2p_z$ orbitals superimposed
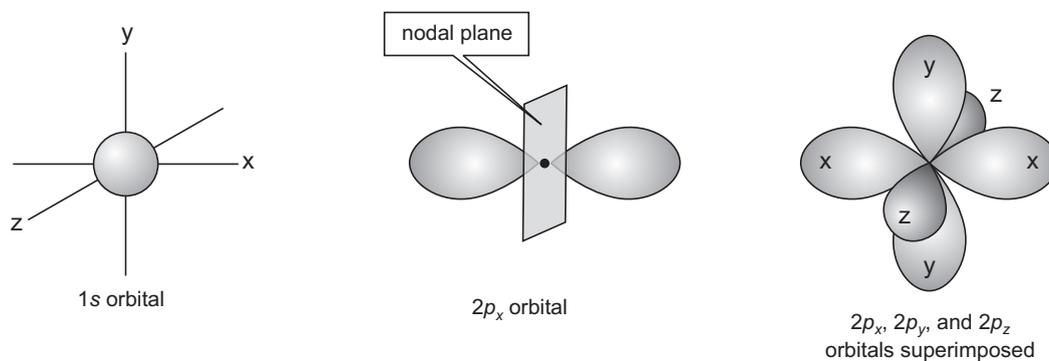
SCHEME 1.1

the wave function ψ. When two parts of an orbital are separated by a node, ψ always has opposite signs on the two sides of the node. With increasing energy, there is an increasing number of nodes. Each orbital can be occupied by a maximum of two electrons of opposite spin (Pauli exclusion principle, Hund's rule).

B. Molecular Orbitals and Bonding

In the molecular orbital method, a bond is formed when two atomic orbitals overlap. Atomic orbitals of the same sign overlap to give a bonding molecular orbital of lower energy. Atomic orbitals of opposite sign give rise to an antibonding molecular orbital of higher energy and containing a node. The number of molecular orbitals is equal to the number of atomic orbitals from which they derive. The overlap of atomic orbitals leads to the formation of sigma and *pi* bonds. Bonds made by overlap along the internuclear axis are called σ bonds (as in H_2, I; HF, II; F_2, III, Scheme 1.2) and those made by overlap of *p* orbitals perpendicular to the internuclear axis are called π bonds. (Scheme 1.2).
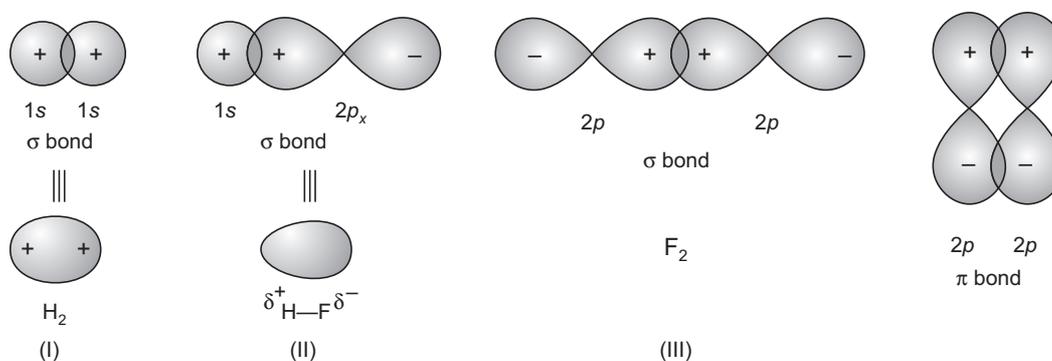
SCHEME 1.2

The hydrogen molecule is cylindrically symmetrical about a straight line drawn through the two nuclei and a cross-section of the molecular orbital when cut perpendicular to the bond axis is circular. This type of molecular orbital is termed σ orbital or σ bond. Similarly in the molecule of H—F, the σ bond is again cylindrically symmetrical about a line passing through the two nuclei. The electrons in the σ bond of H—F are however, not shared equally between the two dissimilar atoms of different electronegativities and unlike in H_2 or F_2 in H—F, the electron distribution is highly polarized (Scheme 1.2).

C. Hybrid Orbitals: Bonding in Complex Molecules

Hybridization of atomic orbitals accounts for observed bond angles and molecular geometries of the molecules.

(*i*) *sp Hybrids give Linear Structures*

In *e.g.*, beryllium hydride BeH_2, formation, consider the following points. In its ground state the beryllium atom has $1s^2\ 2s^2$ electronic configuration. Only a small amount of energy is needed to promote one electron from the $2s$ orbital to one of the $2p$ levels. In the $1s^2\ 2s^1\ 2p^1$ configuration (I, Scheme 1.3) beryllium could enter into bonding, as now two singly filled atomic orbitals are available for overlap. Energy lost in possible promotion of an electron from the $2s$ orbital to one of the $2p$ levels could be regained by bond formation. A bond formation could occur by overlap of the $2s$ orbital of Be with the $1s$ orbital of one H, on the one hand and the $2p$

orbital of Be with second H, on the other (Scheme 1.3). This possible arrangement would give two different bonds of unequal length and at an angle. Theory of electron repulsion, however predicts that compounds like BeH_2 to have linear structure with the bonds to Be of equal length (Scheme 1.3).
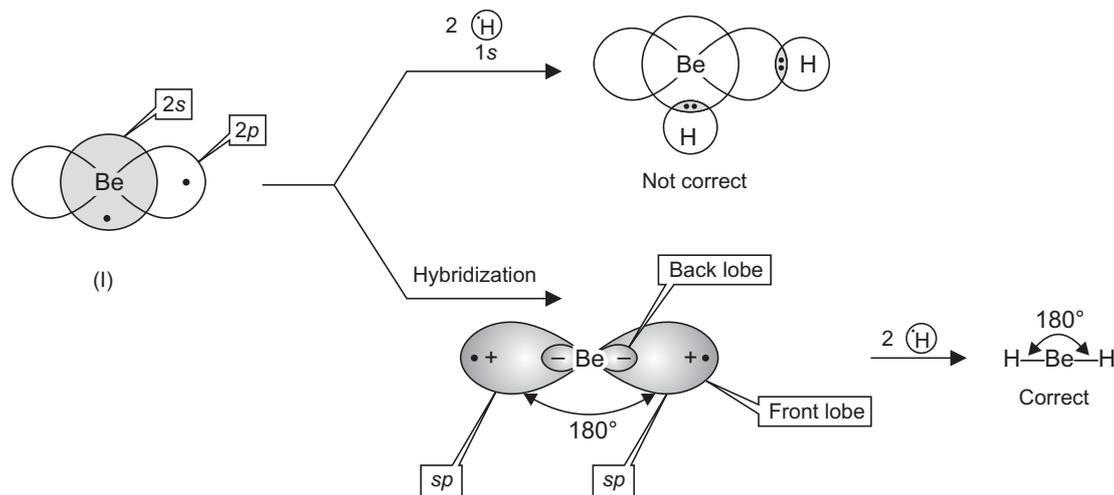


Hybridization in beryllium to create two *sp* hybrids

SCHEME 1.3

A way to explain the geometry of BeH_2 and other molecules is the approach called orbital hybridization. Like mixing of atomic orbitals on different atoms to give molecular orbitals, the mixing of atomic orbitals on the same atom gives new hybrid orbital. In beryllium, mixing the 2*s* and one of the 2*p* wave functions gives two new hybrids, called *sp* orbitals, made up of 50% *s* and 50% *p* character. This process rearranges the orbital lobes in space (Scheme 1.3). The major parts of the orbitals (front lobes) point away from each other at an angle of 180°. There are two additional minor back lobes (one for each *sp* hybrid) with opposite sign. The remaining two *p* orbitals are unchanged and overlap with the two hydrogen 1*s* orbitals gives linear BeH_2.

Thus a 2*s* and a 2*p* orbital mix in a *sp* hybridization to give two linear *sp* hybrids and the remaining two *p* orbitals remain unchanged. This bonding is found both in alkynes and nitriles. The nitrogen and carbon atom of a nitrile group (C≡N) are both *sp* hybridized.
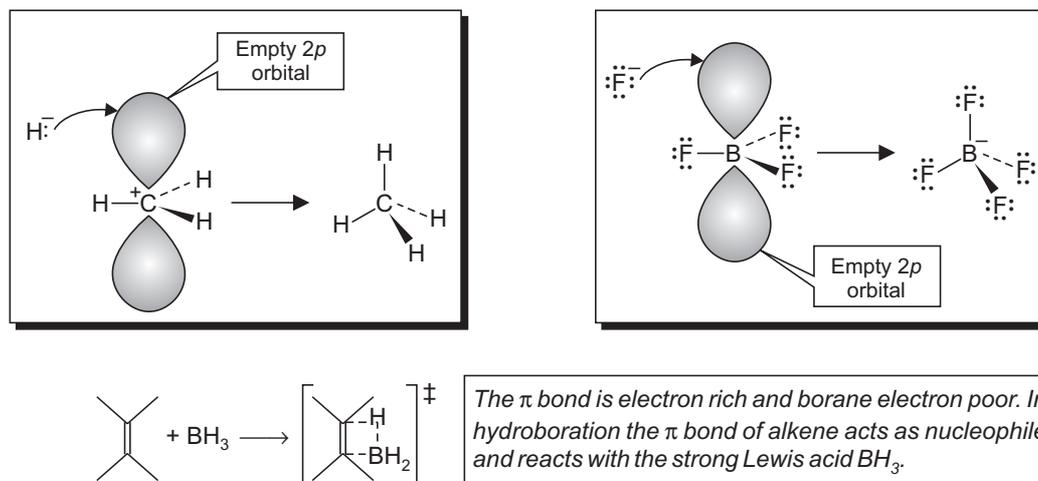
(ii) *sp²* Hybrids give rise to Trigonal Structures

Structure of Borane (BH_3) has a triangular (trigonal planar) shape with the equivalent boron-hydrogen bonds. In its ground state boron has the electronic configuration $1s^2 2s^2 2p^1$. Promotion of a 2*s* electron to one of the 2*p* levels gives three singly filled atomic orbitals (one 2*s* two 2*p*) necessary for the formation of three bonds (Scheme 1.4). Mixing these three orbitals gives three equivalent hybrid orbitals which are sp^2. These have one part the character of an *s* orbital and two parts the character of *p* orbital. These orbitals are pointed toward the corners of an equilateral triangle with angles of 120° between their axes. The formation of borane is via the overlap of each of these three sp^2 orbitals with *s* orbitals of three hydrogen atoms. The sp^2 hybridization also offers a satisfactory model for carbon atoms which form double bonds.
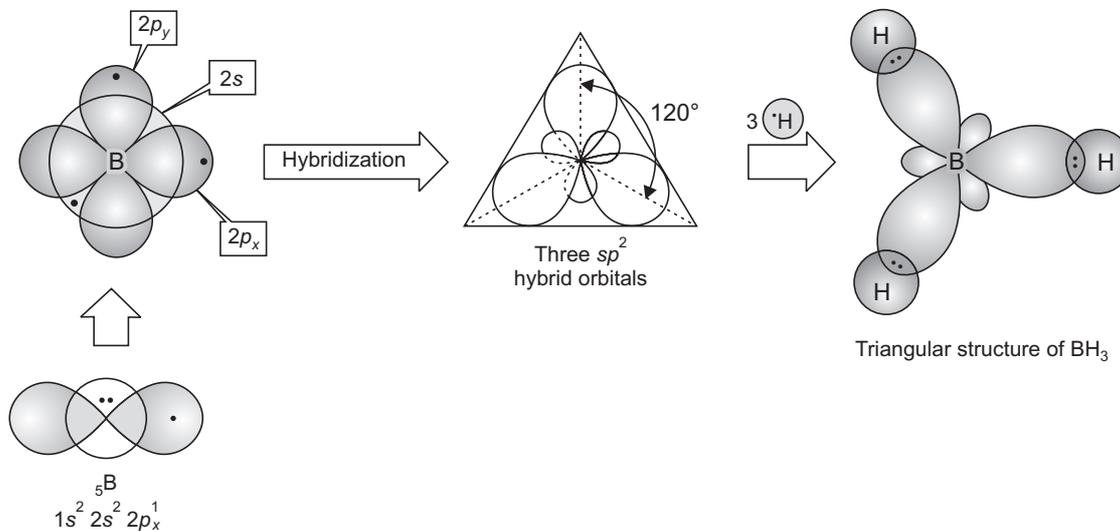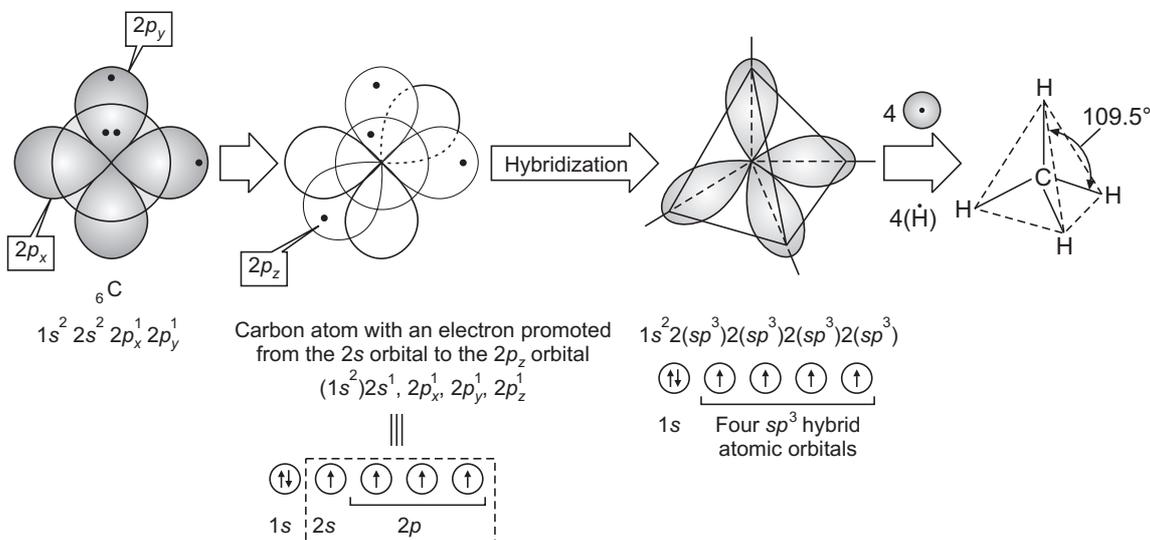
SCHEME 1.4

Trigonal boranes BH_3 and BF_3 have an empty $2p$ orbital. There is no positive charge on these compounds, but both are Lewis acids and react like cations (Scheme 1.4a).

The π bond is electron rich and borane electron poor. In hydroboration the π bond of alkene acts as nucleophile and reacts with the strong Lewis acid BH_3.

SCHEME 1.4a

(iii) sp³ Hybridization gives Tetrahedral Shape

In the case of carbon the promotion of one electron from $2s$ to $2p$ leads to four singly filled orbitals for bonding (Scheme 1.4b). The shape of the four C—H bonds of methane in space with minimum electron repulsion is tetrahedral. For this geometry the $2s$ orbital on carbon is hybridized with all three $2p$ orbitals to give four equivalent sp^3 orbitals with a tetrahedral arrangement (symmetrical arrangement) and each occupied by one electron. The overlap with *e.g.,* four hydrogen $1s$ orbitals gives methane.
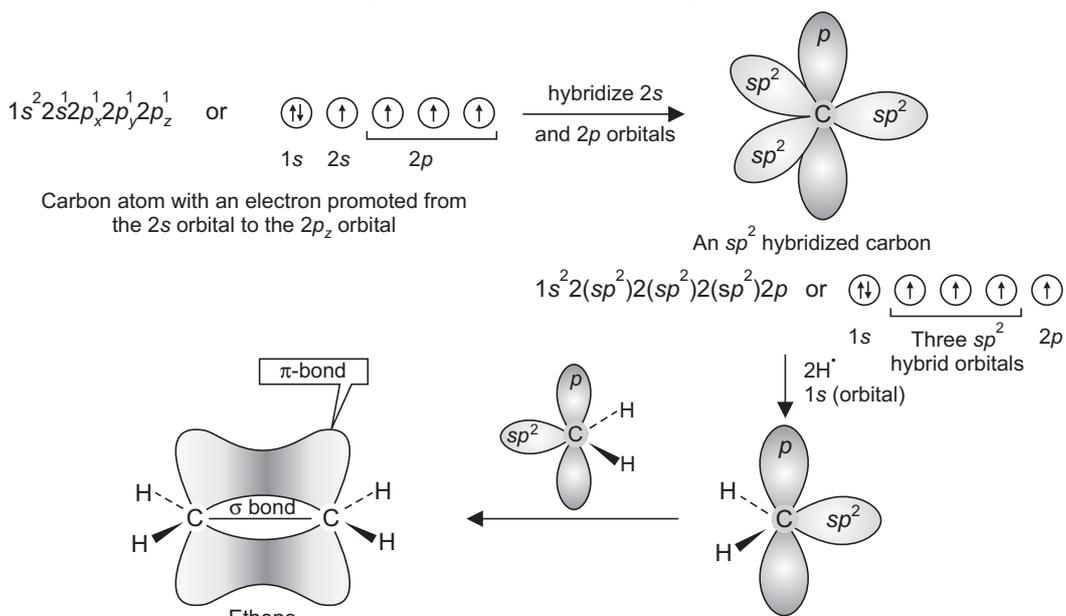
$_6C$

$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$

Carbon atom with an electron promoted from the 2s orbital to the $2p_z$ orbital

$(1s^2)2s^1,\ 2p_x^1,\ 2p_y^1,\ 2p_z^1$

$1s^2(sp^3)2(sp^3)2(sp^3)2(sp^3)$

1s   Four sp^3 hybrid atomic orbitals

1s 2s   2p

Structure of methane, CH_4 showing four equivalent σ bonds (s—sp^3 molecular bond orbitals) and tetrahedral structure

SCHEME 1.4b

A Double Bond

Consider the sp^2 (trigonal) hybridized carbon in e.g., a carbon-carbon double bond in ethene which is a flat molecule with bond angles close to 120°. Hybridization of the 2s orbital and two of the 2p orbitals leads to three equivalent sp^2 hybrid orbitals and one unhybridized 2p orbital (Scheme 1.4c) on each carbon. In ethene the C—C bond is an sp^2–sp^2 molecular σ bond while the C—H bonds are s–sp^2 molecular σ bonds. The π bond results from the parallel overlap through space of the p orbitals.

$1s^2 2s2p_x^1 2p_y^1 2p_z^1$ or

1s 2s   2p

Carbon atom with an electron promoted from the 2s orbital to the $2p_z$ orbital

hybridize 2s and 2p orbitals

An sp^2 hybridized carbon

$1s^2 2(sp^2)2(sp^2)2(sp^2)2p$ or

1s   Three sp^2 2p
hybrid orbitals

$2H^{\cdot}$
1s (orbital)

π-bond

σ bond

H   H
  C   C
H   H

Ethene

SCHEME 1.4c

D. Bond Angles, Shapes of Molecules (VSEPR model) and Reactivity

(i) Structure of Methane

Using the valence-shell—electron-pair repulsion (VSEPR) model, an atom is surrounded by an outer shell of valence electrons. These valence electrons may be involved in the formation of single, double, or triple bonds, or they may be unshared. Each of these combinations leads to a negatively charged region of space, and since like charges repel each other, the various regions of electrons density around an atom is spread out so that each is as far away from the others as possible. The Lewis structure for CH_4 shows a carbon atom surrounded by four separate regions of electron density, each of which consists of a pair of electrons forming a bond to a hydrogen atom. Using a VSEPR model, the four regions radiate from carbon in a way so that they are as far away from each other as possible. This is possible when the angle between any two pairs of electrons is 109.5°. Therefore, all H—C—H bond angles are predicted to be 109.5°, and the shape of the molecule is predicted to be tetrahedral. The H—C—H bond angles in methane as measured experimentally are 109.5°. Thus, the bond angles and shape of methane predicted by the VSEPR model are identical to those observed (Scheme 1.4b).

(ii) Structure of Ammonia and Water

In the molecule of NH_3 the N—H bonds are formed *via* the overlap of an sp^3 orbital of nitrogen with the s orbital of a hydrogen. The lone pair of electrons is on an sp^3 orbital. In nitrogen all the three $2p$ orbitals are available for bonding (Scheme 1.4d), however, direct overlap with $1s$ orbital of hydrogen would give, three N—H bonds perpendicular to each other with bond angles of 90°, the geometry of p orbitals. The bond angles in NH_3 are 107.3°, to show that nitrogen uses hybrid orbitals to form covalent bonds.
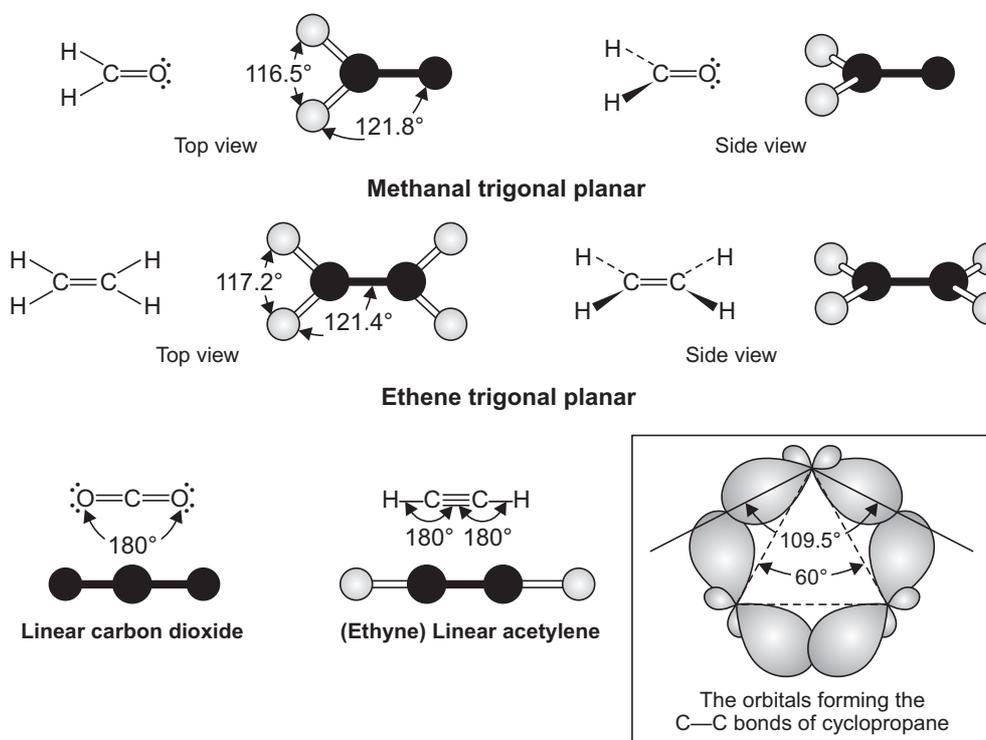

SCHEME 1.4d
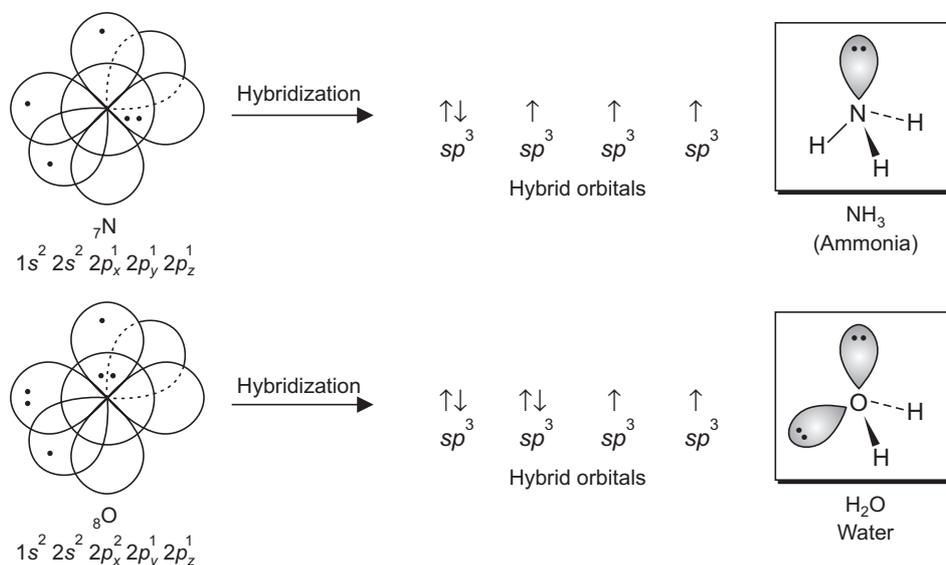
Oxygen has two p orbitals which can be used for bonding. Again as seen in NH_3 an attempt to overlap $1s$ orbitals of two hydrogen atoms would lead to H—O—H angle of 90°. However, the bond angle in water is 104° close to that in NH_3. One can account for the bond angle of 104° in water provided oxygen uses the hybrid orbitals to form covalent bonds (Scheme 1.4d).

The Lewis structure of NH_3 shows nitrogen surrounded by four regions of electron density. Three regions contain single pairs of electrons forming covalent bonds with hydrogen atoms. The fourth region contains an unshared pair of electrons. These four regions of electron density are arranged in a tetrahedral fashion around the central nitrogen atom (Scheme 1.4d). The four regions of electron density (VSEPR model) around nitrogen are arranged in a tetrahedral manner with H—N—H bond angles 109.5°. The observed bond angles are however, 107.3°, this small difference between the predicted and observed angles can be explained due to repulsion between the unshared pair of electrons on nitrogen and the bonding pairs. This repulsion is greater than the electron repulsion between the two bonding pairs.

In water molecule, oxygen is surrounded by four separate regions of electron density. Two of these regions contain pair of electrons used to form covalent bonds with hydrogen; the remaining two contain unshared electron pairs. The four regions of electron density around oxygen (VSEPR model) are arranged in a tetrahedral manner, and the predicted H—O—H bond angle is 109.5°. The actual measured bond angle is 104.5°, a value smaller than predicted and even smaller than in NH_3. The explanation is the same as used to explain bond angles in NH_3, in the case of water the still smaller angle is due to the influence of now two lone pairs on oxygen instead of one on nitrogen.

(*iii*) *Structure of a Double Bond*

A double bond according to the VSEPR model, is treated as a single region of electron density. In formaldehyde (methanal), carbon is surrounded by three regions of electron density, two of which contain single pair of electrons forming single bonds to hydrogen atoms, while the third region of electron density has two pairs of electrons forming a double bond to oxygen. (Scheme 1.4e). In ethene (ethylene) each carbon atom is again surrounded by three regions of

Methanal trigonal planar

Ethene trigonal planar

Linear carbon dioxide

(Ethyne) Linear acetylene

The orbitals forming the
C—C bonds of cyclopropane

SCHEME 1.4e

electron density: two contain single pairs of electrons, and the other contains two pairs of electrons. Three regions of electron density about an atom are farthest apart provided these are in the same plane and make angles of 120° with each other. Thus, the predicted H—C—H and H—C—O bond angles in methanal are 120°; the predicted H—C—H and H—C—C bond angles in ethene are also 120°. Such an arrangement of an atom is called trigonal planar.

(iv) Structure of Linear Molecules

In other types of molecules, a central atom is surrounded by only two regions of electron density. In carbon dioxide *e.g.*, carbon is surrounded by two regions of electron density: each contains two pairs of electrons and forms a double bond to an oxygen atom. Same is the case with ethyne where each carbon is surrounded by two regions of electron density: one contains a single pair of electrons and forms a single bond to a hydrogen atom, and the other contains three pairs of electrons and forms a triple bond to a carbon atom. In each case, the two regions of electron density are farthest apart if they form a straight line through the central atom and generate an angle of 180°. Carbon dioxide and ethyne are therefore, linear molecules (Scheme 1.4e). The bond angle is thus, dependent on the orbital used by carbon in bond formation. The greater the amount of *s* character in the orbital the larger the bond angle. For example, sp^3 hybridized carbons have bond angles of 109.5°, sp^2 hybridized carbons have bond angles of 120°, and sp hybridized carbons have bond angles of 180°. The bond angles of sp^3 carbon are tetrahedral only when the four groups are identical as in CH_4 or CCl_4. In most of the cases the angles deviate a little from the tetrahedral value. For example, the C—C—Br angle in 2-bromopropane is 114.2°. Similarly, slight variations are generally found from the ideal values of 120° and 180° for sp^2 and sp carbon, respectively. These deviations are due to slightly different hybridizations, *i.e.*, a carbon bonded to four other atoms hybridizes one *s* and three *p* orbitals, but the four hybrid orbitals thus formed are generally not exactly equivalent, nor does each contain exactly 25% *s* and 75% *p* character. With the four atoms with different electronegativities, each makes its own demand for electrons from the carbon atom. In strained molecules the bond angles are largely distorted from the normal values.

VSEPR MODEL/SHAPE OF MOLECULES

*One can predict bond angles of molecules and polyatomic ions using Lewis structures and the **valence-shell electron-pair repulsion (VSEPR) model**. The atoms surrounded by four regions of electron density, predict bond angles of 109.5°; by three regions of electron density, predict bond angles of 120° while for two regions of electron density, predict bond angles of 180°. Thus benzene must be a flat hexagon since each carbon in benzene has three areas of electron density around it, thus the carbon atoms are trigonal planar, C—C—C bond angles 120° as well as H—C—C bond angles also 120° and all the carbon atoms in the ring are sp^2 hybridized. Similarly according to VSEPR theory a carbocation e.g., t-butyl cation is predicted to have a trigonal planar geometry (there are three areas of electron density around the central carbon atom).*


(v) Strained Molecules

In cyclopropane (Scheme 1.4e), for geometric reasons, the internuclear C—C—C angle is 60°. The carbon-carbon bonds in cyclopropane have more *p* character than normal sp^3. The orbitals thus, from bent bonds, which are weaker than those in normal alkanes. To compensate for the extra *p* character for C—C bonds extra *s* character is used for the C—H bonds, therefore, these bonds are shorter and stronger than alkyl C—H bonds (C—H bonds in ethane 1.10 Å).

(vi) Role of Bond Angles in Reaction Mechanism

Halocycloalkanes undergo S_N2 reactions, however, with significant rate differences depending on the size of the ring (Table 1.1). The strained cyclopropyl bromide does not undergo substitution, due to prohibitive strain in the transition state. In a S_N2 reaction the reacting carbon adopts an sp^2 configuration as the nucleophile replaces the leaving group (see, Scheme 5.7). The normal bond angle of sp^2 hybridization is 120° and the cyclopropane cannot be squeezed much from 60° (in cyclopropane which has a shape of regular triangle, the internal angle must be 60°).

Table 1.1 Relative reactivities of cycloalkyl bromides in the S_N2 reaction
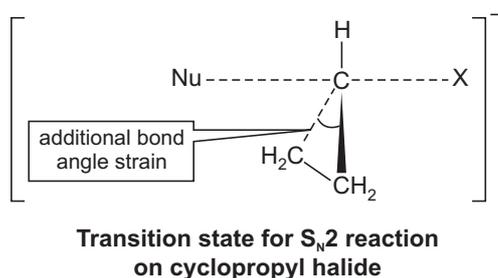
Alkyl Group	Relative Rate
Isopropyl	1.0
Cyclopropyl	negligible
Cyclobutyl	0.008
Cyclopentyl	1.6
Cyclohexyl	0.01
Cycloheptyl	1.0

Transition state for S_N2 reaction on cyclopropyl halide

SCHEME 1.4f

The ring provides a rigid framework which should be capable to tolerate this additional strain. Thus the low reactivity of cyclobutyl bromide is also due to these reasons. Cyclopentyl and cyclohexyl bromides display S_N2 reactivity which is close to their a cyclic counterparts, since these rings are more capable to attain sp^2 hybridization at the reacting carbon (see also Scheme 5.9).

E. Hybridization and Length and Strength of a Bond

Both the length and strength of a carbon-hydrogen bond is dependent on the hybridization of the carbon atom to which the hydrogen is attached. When there is more s character in the orbital used by carbon to form the bond, the shorter and stronger bond results. An s orbital is closer to the nucleus than a p orbital and thus the carbon-hydrogen bond formed by an sp (50% s) hybridized carbon is shorter and stronger than carbon-hydrogen bond formed by an sp^2 (33.3% s) hybridized carbon and this in turn in shorter and stronger than a carbon-hydrogen bond formed by an sp^3 (25% s) hybridized carbon.

The following points may be noted:

- In general shorter bonds are stronger bonds. Increasing s character shortens bonds, thus bonds strength increase with increasing s character.
- More the bonds holding two carbon atoms together, the shorter and stronger is the carbon-carbon bond. Triple bonds are shorter (C≡C, 1.20 Å) and stronger (C≡C, 200 kcal/mol) than double bonds (C=C, 1.33 Å, 152 kcal/mol), which are shorter and stronger than single bonds (C—C, 1.54 Å, 88 kcal/mol).

  Thus double bonds are both shorter and stronger than corresponding single bonds, however, not twice as strong, since π overlap is less than σ overlap. This means that a σ bond is stronger than a π bond. The difference in energy between a single bond, say C—C, and the corresponding double bond is the amount of energy necessary to cause rotation around the double bond.

F. Shapes of Some Reactive Intermediates

A carbocation contains a positively charged carbon atom bearing three substituents to suggest a trigonal planar arrangement as *e.g.,* in *tert*-butyl cation. In a carbocation the carbon is sp^2 hybridized and the unhybridized $2p$ orbital lies perpendicular to the sigma bond framework and has no electrons (is vacant). In BF_3 as well, one has the same situation, the boron atom is sp^2 hybridized and has a vacant p orbital perpendicular to BF_3 plane, and same is the case with BH_3.

tert-Butyl cation

Vacent $2p$ orbital lies perpendicular to plane of carbon atoms

Structure of the methyl anion, $^-$:CH_3

Borane
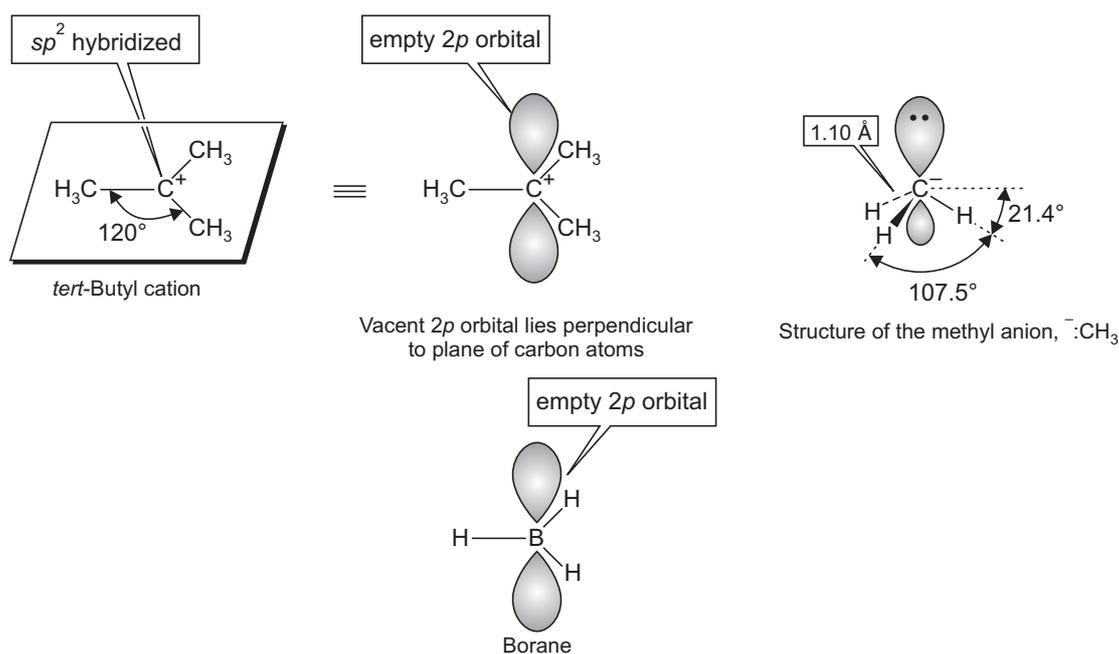
SCHEME 1.4g

A methyl anion has two more electrons than the cation. The orbitals have density at the positively charged nucleus, thus a negatively charged electron would be more stable (lower in energy) in an orbital with more s character. A pyramidal structure seems reasonable for the methyl anion however, the molecule is not a perfect tetrahedron. Hybridization and bond angles are closely related. With more s character in the orbital containing the nonbonding electrons, the pyramidal shape is likely to increase.

As per the calculations the structure of methyl anion is as shown (Scheme 1.4g). With the three sigma bonds and a lone pair, a carbanion is electronically similar to an amine. Consider the hybridization change on formation of methyl radical from methane (Scheme 1.4h). At present it is however not possible to choose between a planar or a pyramidal structure for a free radical *e.g.,* for neutral methyl radical which can be obtained by the removal of hydrogen atom from methane. Spectral measurement have however, shown that methyl radical has nearly planar configuration described by sp^2 hybridization with unpaired electron in the remaining p orbital perpendicular to the molecular plane (Scheme 1.4h). In the pyramidal arrangement, the carbon would be sp^3 hybridized and odd electron would occupy an sp^3 hybridized orbital in one corner of the tetrahedron.
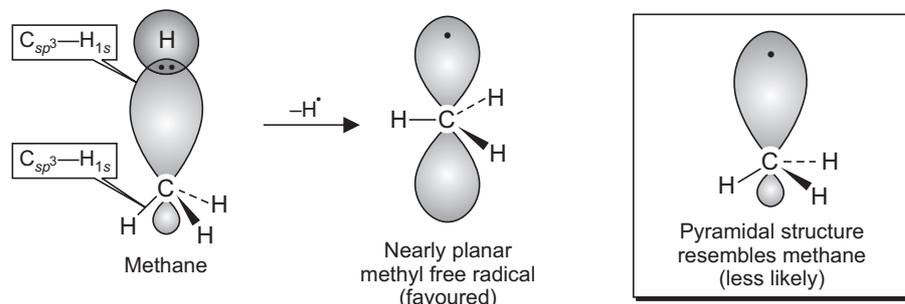
Hybridization change on forming methyl radical from methane
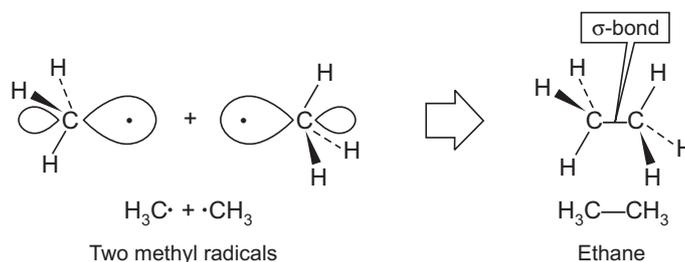
SCHEME 1.4h

G. Hyperconjugation

The planar structure of methyl and other alkyl radicals helps to explain their relative stabilities by hyperconjugation (Scheme 1.4*i*). Thus there is a conformer in *e.g.,* ethyl radical in which C—H bond of the CH_3 group is aligned and overlaps with one of the lobes of singly occupied *p* orbital on the radical centre. Thus the bonding pair of electrons in the σ orbital spread into the partly empty *p* lobe a phenomenon known as hyperconjugation. Like resonance, hyperconjugation is also a form of electron delocalization which are distinguished by the type of orbital. Resonance generally refers to π type overlap of *p* orbitals, while hyperconjugation involves overlap with the orbital of σ bonds. With the increase in number of alkyl groups, the number of hyperconjugation interactions increases as in isopropyl group (more details are in sec. 2.14).

Hyperconjugation in ethyl radical
($\dot{C}H_2$—CH_3)
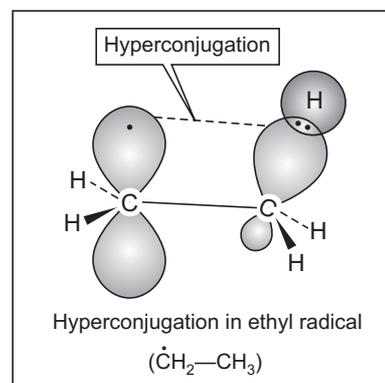
SCHEME 1.4i

H. Sigma and *pi* Bonds

A C—C sigma bond is formed by the overlap of hybrid orbitals. In ethane *e.g.,* this bond consists of two sp^3 hybrids, when these roughly sp^3 hybridized carbons approach for the overlap of singly occupied orbitals (Scheme 1.4*j*).

$H_3C\cdot$ + $\cdot CH_3$

Two methyl radicals

H_3C—CH_3

Ethane

SCHEME 1.4j

Bonds made by overlap along the internuclear axis are called σ bonds, while those made by overlap of *p* orbitals perpendicular to the internuclear axis are called *pi* bonds (Scheme 1.4*k*).

In contrast to the sigma orbital, the *pi* molecular orbital has zero electron density along the molecular axis, but has the maximum electron density above and below the internuclear line. All the sigma bonds around the *pi* bonds are coplanar, the bond angles being 120°. The plane of the molecule is the nodal plane of the *pi* bond.
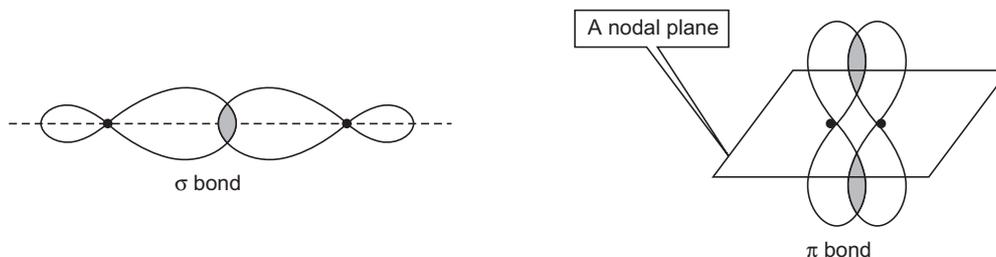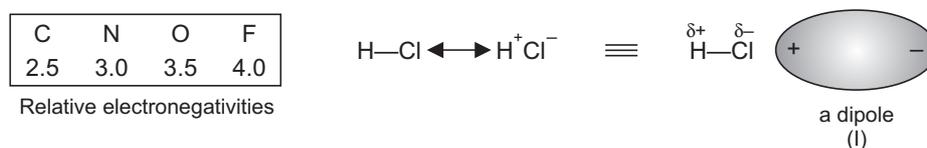

SCHEME 1.4k

1.2 ELECTRONEGATIVITY—DIPOLE MOMENT

Carbon is unique among the elements, since it is able to form a huge number of compounds by bonding to itself and to the atoms of other elements *e.g.,* hydrogen, oxygen, nitrogen, sulphur and the halogens. This bonding is almost always covalent.

The sharing of electrons in a covalent bond is not exactly equal when the linked elements are different. The relative attractive power exerted by an element on the electrons in a covalent bond can be expressed by its electronegativity. According to one quantitative definition of electronegativity, there is an increase in electronegativity along the series towards fluorine as shown (Scheme 1.5).

Hydrogen with electronegativity 2.0 is close in this respect with carbon (for further details on electronegativity see, Scheme 3.9). When two atoms with different electronegativities form a covalent bond, the atom with greater electronegativity draws the electron pair to it and a polar covalent bond results as in hydrogen chloride and can be represented by the usual symbol (I, Scheme 1.5) when necessary. In fact the hydrogen chloride molecule is a resonance hybrid of two resonating structures.
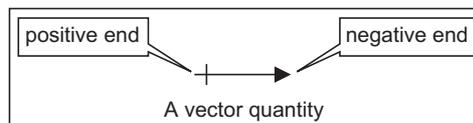

SCHEME 1.5

As a consequence of a partially positive end (δ^+) and a partially negative end (δ^-) in HCl molecule represents a dipole (II, Scheme 1.5) and therefore, has a dipole moment (a physical property). Thus the dipole moment is a property of the molecule which is due to charge separations. It is defined as the product of the magnitude of the charge (e) in electrostatic units (esu) and the distance (d) which separates them in centimeters (cm):

$$\mu = e \times d$$

Dipole moments are typically of the order of 10^{-18} esu cm, since charges are typically of the order of 10^{-10} esu and the distance is of the order of 10^{-8} cm. For convenience this unit (1×10^{-18} esu cm) is defined as one Debye (abbreviated D). The direction of polarity of a polar bond is usually symbolized by a vector quantity (Scheme 1.6).
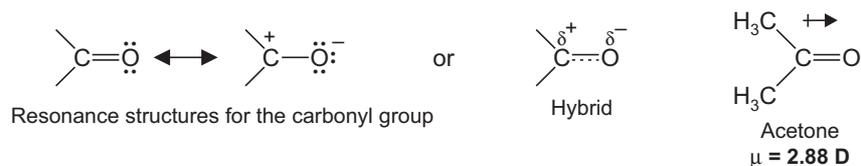

Scheme 1.6

The arrow head points to be the negative part of the molecule, while the crossed end is the positive end. A molecule with polar bonds, may, however, not possess a dipole moment *i.e.,* the molecule itself may be non-polar. This is so when a particular molecule has a shape (or symmetry) so that the dipoles of the individual bonds cancel each other. Thus one is concerned with the total moment of the molecule which is the vectorial sum of the individual bond moments as *e.g.,* in the case of 1, 2-dichloroethene isomers (Scheme 1.7).


vector sum = ↥	vector sum = 0
μ = 2.95 D	μ = 0
b.p. = 60°C	b.p. = 48°C
cis-1, 2-dichloroethene	*trans*-1, 2-dichloroethene
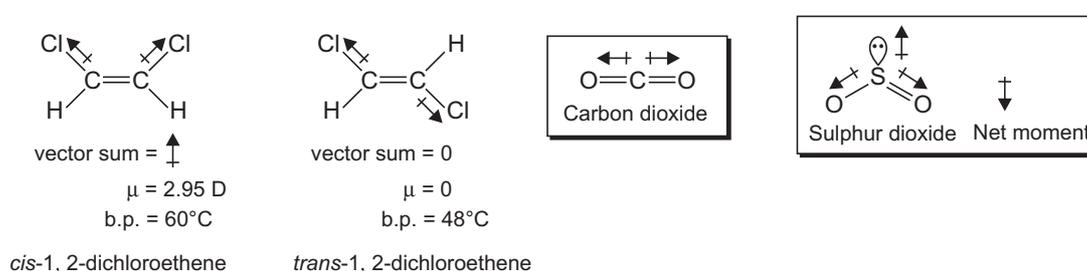
SCHEME 1.7

Similarly carbon in CO_2 is *sp* hybridized and the molecule is linear. The C—O bond moments oppose each other and cancel, in SO_2 however, S is sp^2 hybridized with two σ bonds to O and one with unshared electron pair. The O—S—O bond angle is around 120° and S—O moments do not cancel. Thus unlike CO_2, SO_2 has μ = 1.6 D.

The carbonyl group is polar. The carbon atom is bonded to the more electronegative oxygen atom. The resulting imbalance in the electron density leads to a permanent dipole of 2–3 Debyes (D) in the case of simple carbonyl compounds (Scheme 1.8).


Resonance structures for the carbonyl group   Hybrid   Acetone
μ **= 2.88 D**

SCHEME 1.8

2-chloroethanol is much more acidic than ethanol. This can be explained due to electrostatic interaction of the C—Cl dipole with the negative charge of the alkoxide ion (Scheme 1.9). The negative charge on oxygen is nearer to the positive end of the dipole than it is to the negative end. Consequently, electrostatic attraction exceeds repulsion, leading to the stabilization of the anion. This stabilization of the anion increases its ease of formation and the conjugate acid, 2-chloroethanol, is more acidic than ethanol itself.


2-chloroethanol
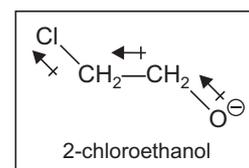
SCHEME 1.9

In the equilibrium for 2-halocyclohexanones (Scheme 1.10) there is an increase in the per cent of axial conformer on going from 1, 4-dioxane to heptane as solvent. The C—Cl and C=O dipoles reinforce each other in the equatorial form, however, these cancel to some extent in the axial form. Thus the equatorial form is more polar and should be favoured by the more polar solvents.

The equatorial form is more polar

Halogen	% Axial (heptane)	% Axial (1, 4-dioxane)
Br	85	62
Cl	76	37

2-halocyclohexanones
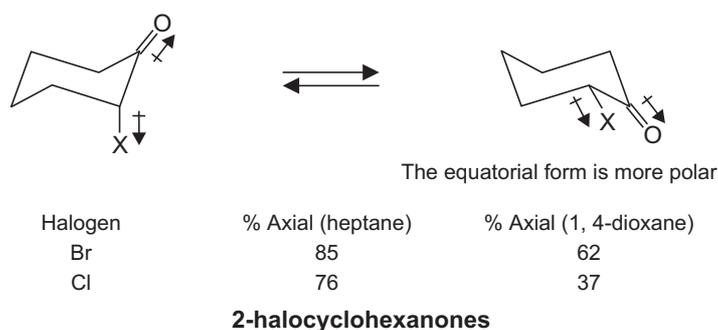
SCHEME 1.10

To cite one example of the involvement of carbon-halogen dipole is the electrophilic aromatic substitution in a halobenzene. A halogen is *o*, *p* — directing substituent. Substitution at the *meta* position of a halobenzene can lead to three resonance structures (Scheme 1.11). All the three structures are strongly destabilized by electrostatic interaction of the positive charge in the ring with the carbon-halogen dipole. As a consequence the *meta* position in a halobenzene is strongly deactivated. Though similar situation is also obtained during *o* and *p* attack, however, in these cases additional stable halonium ion structures make the *o*, *p* attack for more facile (Scheme 8.42).


Reaction at the *meta* position

C—X
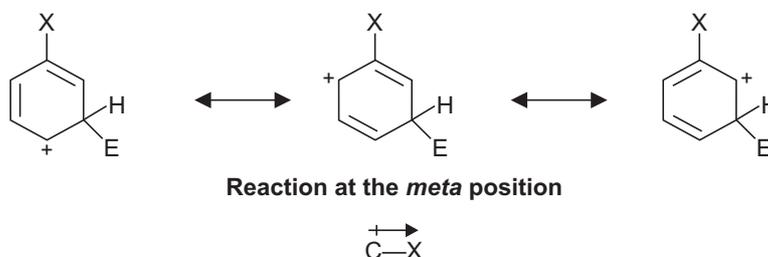
SCHEME 1.11

## 1.3 INDUCTIVE AND FIELD EFFECTS

One may observe a change in the rate constant or equilibrium constant of a reaction by replacing a hydrogen atom by another atom or group of atoms. These substituent effects may be the result of the size of the substituent (steric effect) and/or its influence on the availability of electrons (electronic effect) on the site of the reaction. The electronic effect which a substituent can exert may be either electron releasing or electron withdrawing. These electronic effects are further subdivided into an inductive and a resonance (mesomeric effect). The inductive effect (I) is a result of a substituents' intrinsic ability to supply electrons (electron donation, $+I$ effect) or withdraw electrons (electron withdrawing) $-I$ effect, *i.e.,* the inductive effect depends

on the electronegativity of the substituent. The inductive effect is transmitted through σ bonds and weakens as the distance between the substituent and the reactive center increases. Thus the effect is greatest for the adjacent bond and may be felt weakly farther away (see, Scheme 3.18). The effect may be represented for ethyl chloride (Scheme 1.12). In this case chlorine atom has –*I* effect and thus C-1 atom looses some of its electron density and as a result C-1, Cl bond is polarized and a slight positive charge is generated on C-2. In this way the replacement of hydrogen atom by a more electronegative atom results in electron displacements throughout the molecule.
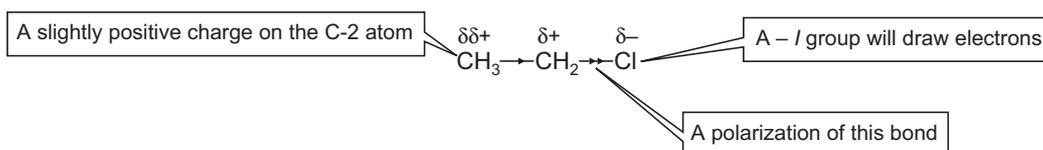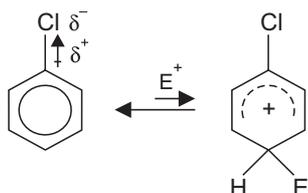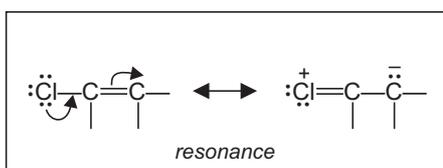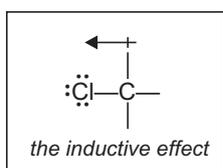

SCHEME 1.12

The other effect operates through space (and not through σ bonds) or through solvent molecules and is called the field effect. Normally the field effect depends on the geometry of the molecule whereas the inductive effect depends only on the nature of the bonds. As an example of the field effect (long range polar interactions) the two acids (I and II, Scheme 1.13) have different pK_a values. The inductive effect of the chlorine atoms on the position of the electrons in the COOH group must be same since the same bonds intervene. Consequently, the acidity must have been equal. However, this difference in pK_a value shows the operation of field effect, since the two chlorine atoms are placed closer in space to the COOH group in I than in II.
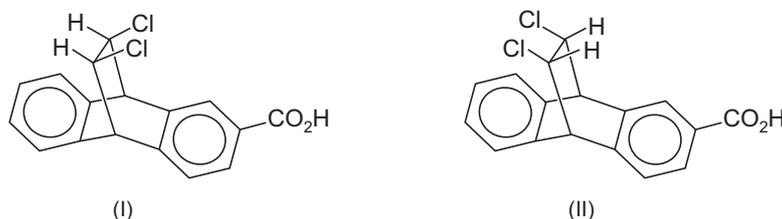
SCHEME 1.13

The inductive effect (+*I*) of alkyl group has been invoked to explain the carbocation stability. This effect also helps in explaining the orientation and reactivity during electrophilic substitution on benzene derivatives (Sec. 8.8).

The resonance effect (see, Schemes 2.14 and 2.15) involves delocalization of electrons through resonance via the π system. Atoms and functional groups may be arranged according to their ability to donate or withdraw electrons. The inductive and resonance effects of many groups are in the same direction. Other groups display opposite effects in the two cases. Normally atoms which are more electronegative than carbon and which also have non-bonding electrons possess opposing characteristics. The halogens illustrate these opposing effects (Scheme 1.14). A good example is found during electrophilic substitution when the inductive effect of a halogen on the benzene ring slows the rate of further substitution (Scheme 1.14).
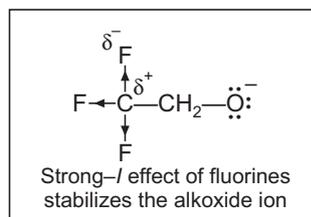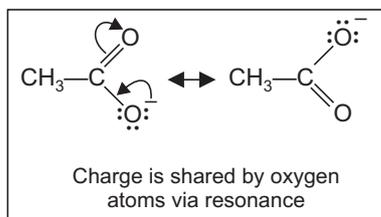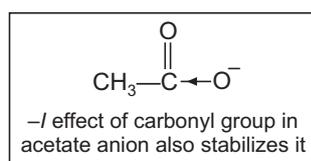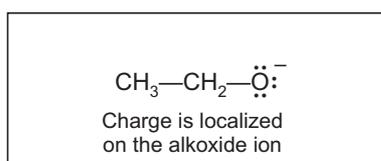
the inductive effect

resonance

The C—Cl bond is strongly polarized. The δ^+ on the carbon slows a substitution reaction which places more positive charge on the ring. A halogen, however denotes electrons in the ring via resonance. Thus a halogen in o, p director.

SCHEME 1.14

EXERCISE 1.1

How one can explain that acetic acid (pK_a = 4.7) is stronger acid than 2, 2, 2-trifluoroethanol (pK_a = 12.8) and ethanol is the least acidic (pK_a = 15.9) from among these three compounds?

ANSWER. *Consider the species after the loss of a proton from each of these compounds. In the case of ethanol the negative charge resides on its single oxygen i.e., the charge is localized (Scheme 1.14a). In the carboxylate ion both inductive withdrawal of electrons and the ability of two atoms to share the negative charge via resonance renders the conjugate base of the carboxylic acid more stable than the conjugate base from ethanol. 2, 2, 2-Trifluoroethanol is much stronger acid than ethanol, since in the former the highly electronegative fluorines help in the stabilization of its alkoxide ion.*


$CH_3—CH_2—\ddot{O}\!:^-$

Charge is localized on the alkoxide ion

–*I* effect of carbonyl group in acetate anion also stabilizes it

Charge is shared by oxygen atoms via resonance

Strong–*I* effect of fluorines stabilizes the alkoxide ion

SCHEME 1.14a

EXERCISE 1.2

Acidity order of alcohols in aqueous solution is :

$CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$. *Can inductive effect explain this order?*

ANSWER. *Electron donating inductive effect (+ I) of alkyl groups will retard the formation of an alkoxide to reduce the acidity of an alcohol. Thus t-Butanol is the weakest acid (Scheme 1.14b).*

However, in the gas phase it is found that the acidity order of alcohols is opposite to that found in solution. Thus it is probably not the + I effect of alkyl groups that is important but stabilizing effect of the solvent. A smaller alkoxide ion is approached more easily by the solvent to solvate it (see Scheme 3.18).
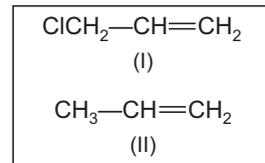
$$\delta+ \quad \delta-| \\ H_3C \rightarrow C—O^- \\ |$$

The electron donating inductive
effect destabilizes the
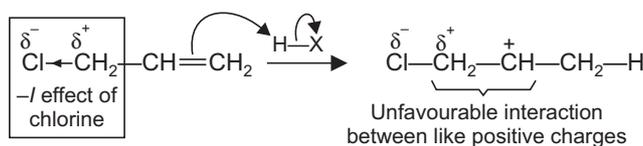alkoxide ion
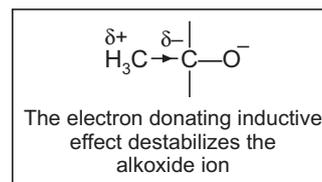
SCHEME 1.14b

EXERCISE 1.3

Which of the alkenes (Scheme 1.14c) is expected to react faster with HX?

ANSWER. *Consider the protonation of the double bond in (I, Scheme 1.14c) which is according to Markovnikov rule.*

$ClCH_2—CH{=}CH_2$
(I)

$CH_3—CH{=}CH_2$
(II)

SCHEME 1.14c

$$\overset{\delta^-}{Cl}\leftarrow\overset{\delta^+}{CH_2}—CH{=}CH_2 \xrightarrow{\;H—X\;} \overset{\delta^-}{Cl}—\overset{\delta^+}{CH_2}—\overset{+}{CH}—CH_2—H$$

–I effect of
chlorine

Unfavourable interaction
between like positive charges

SCHEME 1.14d

Due to the –I effect of chlorine a positive charge on the methylene group would be in opposition to the expected carbocation formed during the addition of HX. No such effect is operative in (II).

EXERCISE 1.4

Discuss in terms of resonance and inductive effect the addition of HX to methyl vinyl ether.

ANSWER. *The –I effect of oxygen generates a partial positive charge on the adjacent carbon, which will get enhanced on protonation (Markovnikov rule) during the*

first step of addition of HX i.e., during the formation of intermediate carbocation which is an unfavourable situation. However, resonance stabilization dominates the inductive effect and the addition occurs smoothly (Scheme 1.14e).
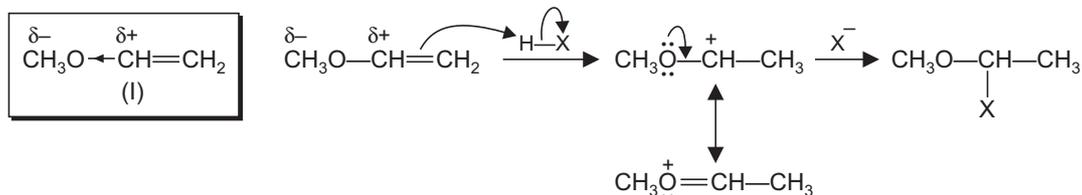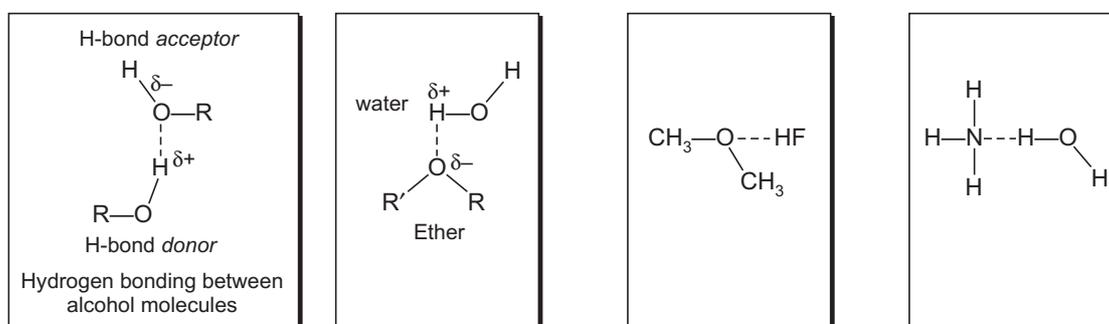
SCHEME 1.14e

1.4 HYDROGEN BOND

The hydrogen atom which is bonded to an electronegative atom can form a hydrogen bond to a second electronegative atom. The hydrogen bond, is thus a force of attraction between opposite partial charges, *e.g.,* δ^+ charge on H in the OH group and δ^- charge on the O of another group (Scheme 1.15).

No such partial charges exist in the molecules of alkanes since C and H have nearly same electronegativities. Only three elements, F, O and N, have atoms that are electronegative enough to participate significantly in hydrogen bonds. A hydrogen bond requires a hydrogen bond donor and a hydrogen bond acceptor as in the alcohol molecule (Scheme 1.15).
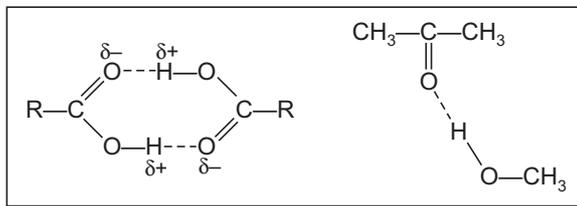
SCHEME 1.15

An ether has no O—H proton, therefore, the ether group cannot donate hydrogen bonds and thus cannot form a hydrogen bond with another ether molecule. Since, ether molecules are not held together by hydrogen bonds, they are more volatile than alcohols of the same molecular weight. The oxygen of the ether group can however, form hydrogen bonds with an alcohol or a other hydrogen bond donor *e.g.,* water (Scheme 1.15). So ethers are more soluble in water than in alkanes. The hydrogen bond is conventionally represented by a dotted line.

The hydrogen bond (bond dissociation energy about 1–9 kcal/mol) is weaker than an ordinary covalent bond. When there are many such bonds as in carbohydrates, the total strength

is very great. The bond may be formed both between molecules of the same type as in alcohols (Scheme 1.15) and carboxylic acids (Scheme 1.16) and molecules of different type as in an ether and alcohol (Scheme 1.15) or as in the interaction between the proton of an alcohol and the oxygen of a carbonyl group. Two types of hydrogen bonding have been recognized: intramolecular (within the same molecule) and intermolecular (between two or more molecules).

SCHEME 1.16

Due to hydrogen bonding, there is an increase in intermolecular 'aggregation' forces which is reflected in the boiling point and solubility of the organic compound. There is an increase in the boiling point since energy is required to separate the hydrogen bonded molecules in their translation to the gaseous state. Hydrogen bonds exist in the liquid and solid phases and in solution. Compounds which form strong hydrogen bonds may be associated even in the gas phase. Thus acetic acid exists as a dimer in the gas phase.

Intramolecular hydrogen bonds may also be formed and these have particular significance. When the resulting ring is five or six membered then the phenomenon is termed chelation. An example of chelation is for the enolic form of acetylacetone (Scheme 2.50). Since on chelation, intermolecular aggregation forces are not operative, chelated compounds have normal boiling points (Scheme 1.17). Thus, *o*-nitrophenol is much more volatile than its *p*-isomer, since only the latter can form intermolecular hydrogen bonds.

o-nitrophenol
(more volatile because of
intramolecular hydrogen bonding)

p-nitrophenol
(less volatile because of intermolecular hydrogen bonding)
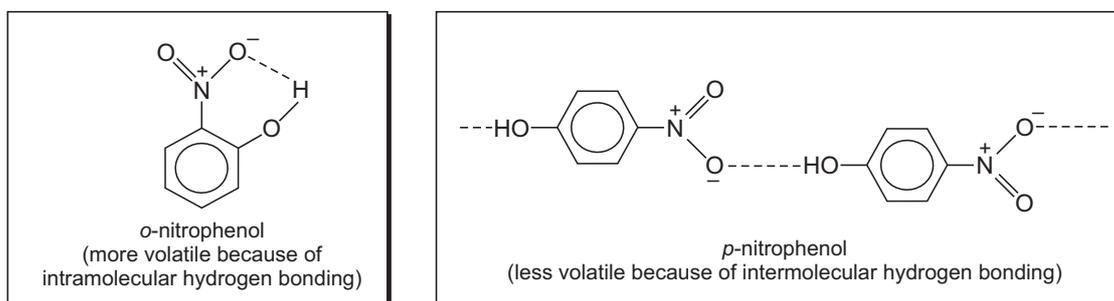
SCHEME 1.17

An important way to detect hydrogen bonding is *via* IR and NMR spectroscopy. A free OH group of an alcohol or a phenol shows a sharp infrared absorption around 3600 cm^{-1} (O—H stretching vibrations). On hydrogen bonding the band becomes broad and is shifted to lower frequencies (around 3400 cm^{-1}). In several cases in dilute solutions, there may be partial hydrogen bonding, *i.e.,* some hydroxyl groups are free and others bonded. In these cases one therefore, observes two bands, one sharp band at high frequency (around 3600 cm^{-1}) and another broad band at lower frequency (around 3400 cm^{-1}). A distinction can also be made between inter- and intramolecular hydrogen bonding on the basis of infrared spectroscopy. In very dilute solution, formation of intermolecular hydrogen bonds does not take place as the molecules are widely separated. Increasing the concentration of the alcohol or phenol causes the sharp band around 3600 cm^{-1} to be replaced by a broad and lower frequency band which is assigned to OH groups that are associated through intermolecular hydrogen bonding. Intramolecular hydrogen bonds remain unaffected and as a result the absorption band also remains unaffected. In the case of *o*-nitrophenol the OH band (intramolecular hydrogen bonding) is at 3200 cm^{-1} in

KBr pellet as well as in CHCl$_3$ solution, whereas in the *p*-isomer, the values are different in the two media KBr (pellet 3330 cm^{-1}; CHCl$_3$ solution 3520 cm^{-1}). In the ^{1}H NMR spectrum a hydrogen bonded hydroxyl group shows a downfield shift of its proton.

EXERCISE 1.5

(a) Why the O—H stretching frequency for t-butyl alcohol is a more sharper band compared with methanol?
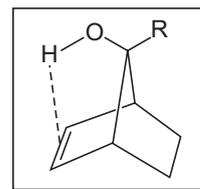
(b) Which of the following norbornane systems can be detected by IR spectroscopy:

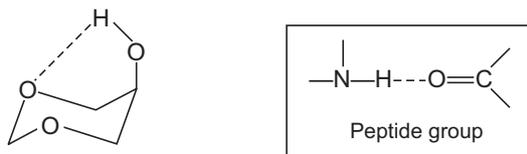| (I) | (II) | (III) |
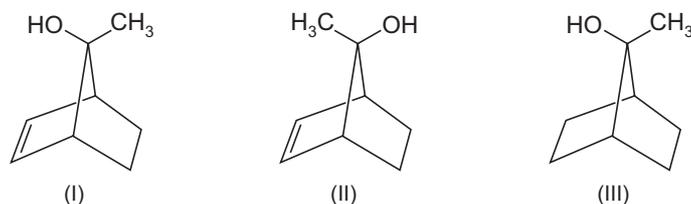
SCHEME 1.18

ANSWER. *(a) Due to steric effects it is far more difficult for t-butyl alcohol to involve in intermolecular hydrogen bond formation.*

(b) In (I, Scheme 1.18a), intramolecular hydrogen bonding would be detected.

SCHEME 1.18a

Hydrogen bonding effects structure (chemical properties) and molecular shape of molecules. Thus *e.g.,* the role of intramolecular hydrogen bonding is reflected in the large amount of enol present in some tautomeric equilibria (see, Scheme 2.48). It also influences conformation of molecules. The six membered heterocycles of oxygen closely resemble the chair conformation of cyclohexane. In heteroxyclic rings the steric repulsions for axial substituents are reduced due to the replacement of a methylene groups of cyclohexane by oxygen or nitrogen. Since the divalent oxygen has no substituents, therefore, the 1, 3-diaxial interactions which are the main unfavourable interactions for axial substituents in cyclohexanes are absent (Scheme 1.18). With the presence of a polar substituent, interactions between the substituent and the ring heteroatom can become important. Thus, the preferred conformation of 5-hydroxy-1, 3-dioxane (Scheme 1.18*b*) has the hydroxyl group in the axial position. This conformation is favoured due to hydrogen bonding of the hydroxyl group with the ring oxygen which is possible only with the axial hydroxyl group to serve as a stabilizing force for this conformation.

Peptide group

SCHEME 1.18b