→ Organic chemistry :→

→ Structure and bonding :→

→ Hybridisation :→

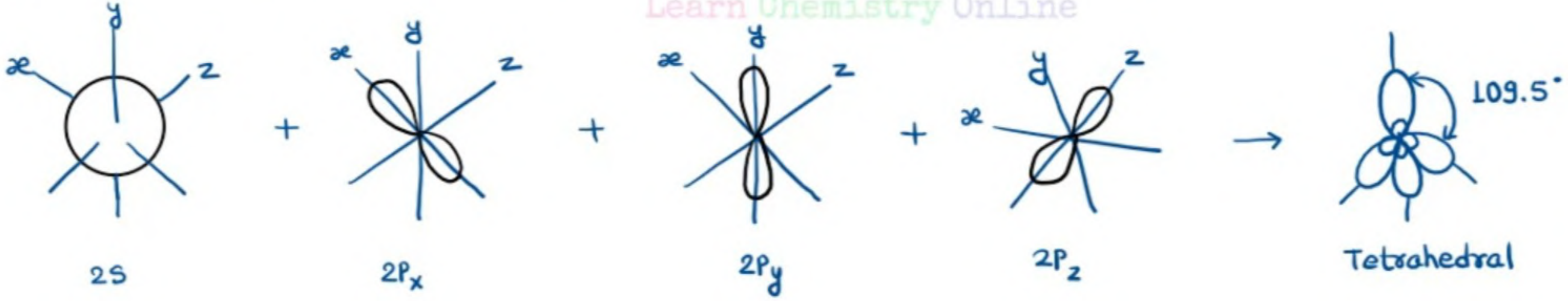
- Hybridisation may be defined as the mixing of two or more than two atomic orbitals of an atom having comparable energy to give an equal number of identical orbitals having same energy and shape.
- All hybrid orbitals are oriented symmetrically to have maximum distance from each other.

→ Types of hybridisation :→

- Carbon atom undergoes three types of hybridisation depending upon the number and type of orbitals mixing together.

1. sp^3 or Tetrahedral hybridisation :→

- One s and three p orbitals mix to form a set of four identical orbitals called sp^3 hybrid orbitals which are directed towards the four corners of tetrahedron.
- All saturated hydrocarbons contain sp^3 hybrid carbon atoms.
- sp^3 hybrid orbitals has 25 % s-character and 75 % p-character.

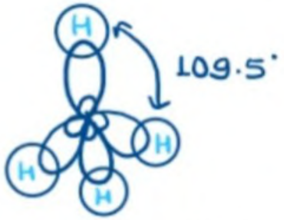


→ Shape of CH_4 molecule:→

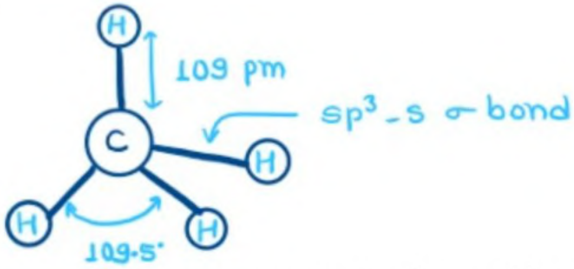
$_6C = 1s^2\ 2s^2\ 2p^2$

Ground state → $\underset{2s}{\boxed{1L}}\ \underset{2p}{\boxed{1\,|\,1\,|\ \ }}$

Excited state → $\underbrace{\underset{2s}{\boxed{1}}\ \underset{2p}{\boxed{1\,|\,1\,|\,1}}}_{sp^3}$

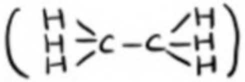


Orbital picture of CH_4

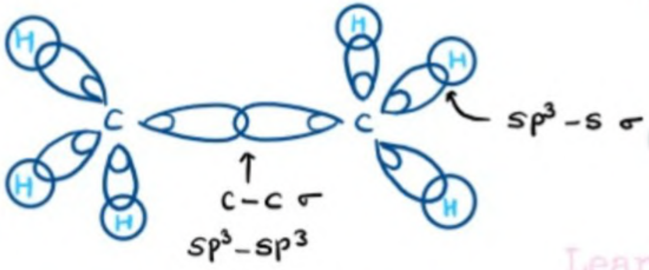


Ball and stick model of methane

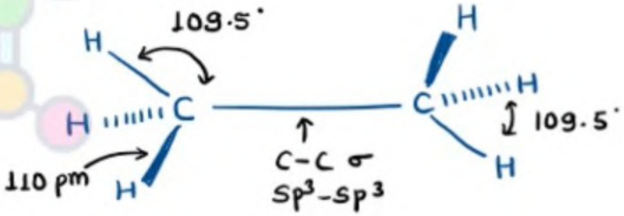
→ Shape of C_2H_6, Ethane:→



$$\left(H_3C-CH_3\right)$$



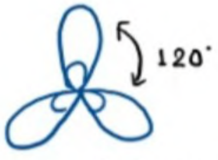
Orbital picture of ethane



structure of ethane

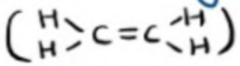
2. sp^2 or Trigonal hybridisation:→

- One s and two p orbitals of carbon atom mix to give set of three sp^2 hybrid orbitals.
- Bond angle 120°
- All compounds with C=C bonds have sp^2 hybridised carbon atoms.
- Each hybrid orbital has 33% s-character and 66% p-character.

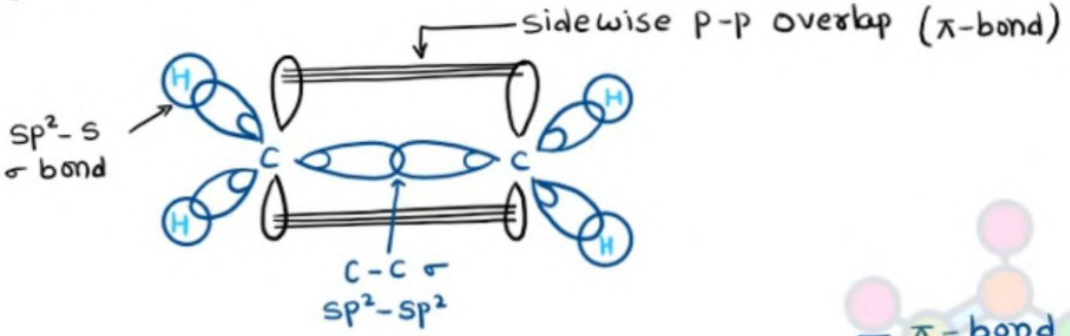


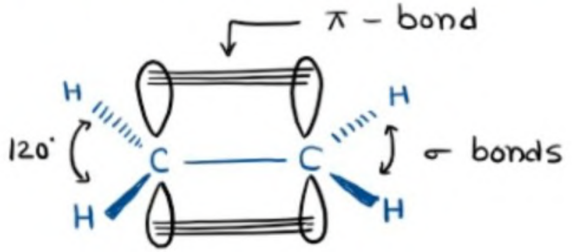
Planar triangular

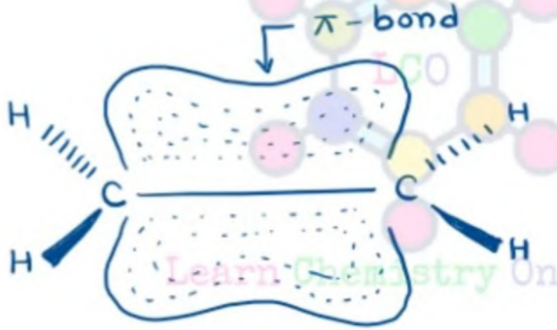
- The remaining unhybridised p orbital is always perpendicular to plane containing three sp^2 hybrid orbitals.

→ Shape of ethylene molecule, C_2H_4 :→ 
$\left(\begin{smallmatrix}H\\H\end{smallmatrix}\!>C=C<\!\begin{smallmatrix}H\\H\end{smallmatrix}\right)$

- Ethylene has two electron pairs shared b/w two C-atoms. This bond is called carbon-carbon double bond.







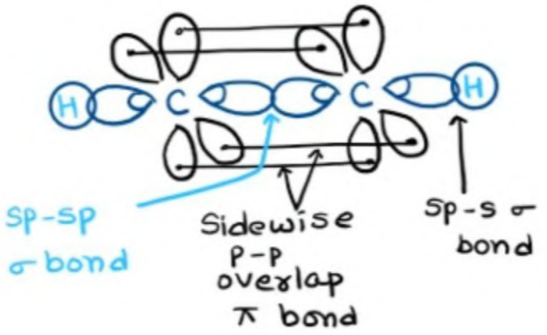
- The carbon-carbon double bond is made up of a σ-bond and a π-bond.
- The bond energy of a Carbon-carbon π-bond is about 251 KJ mol^{-1} and therefore, it is weaker than a Carbon-carbon σ-bond which possesses 347 KJ mol^{-1} of energy.
- As the carbon atoms are held more tightly, the C=C bond length in ethylene is shorter (134 pm) than the C-C bond length in ethane (154 pm).
- The bond energy for C=C bond ($\sigma + \pi$) in ethylene is 598 KJ mol^{-1} and that for C-C bond in ethane is 347 KJ mol^{-1}.

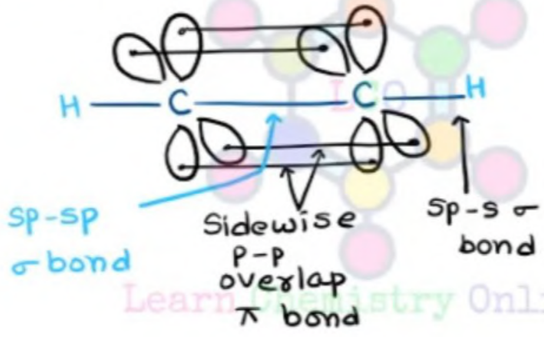
3. sp or diagonal or Linear hybridisation :→

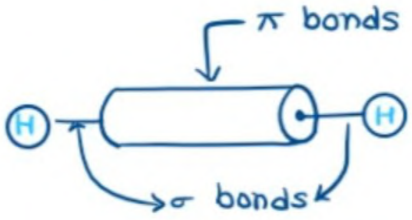
- These hybrid orbitals are formed by mixing of a carbon 2s orbital with one of the 2p orbitals.
- The two sp-hybridised orbitals are directed in opposite directions at an angle of 180°.
- The remaining two unhybridised p orbitals are always perpendicular to each other and also to the two sp hybridised orbitals.
- Each sp hybrid orbital has 50% s-character and 50% p-character.

→ Shape of acetylene molecule, C_2H_2 :→ ($H-C\equiv C-H$)

- Acetylene molecule has three electron pairs shared between two carbon atoms. This bond is called carbon-carbon triple bond.







- It is clear from figure that a molecule of acetylene should be linear. This is supported by physical measurements, i.e., H-C-C bond angle is 180°. The $C\equiv C$ and C-H bond lengths in acetylene are 120 and 106 pm, respectively.
- The $C\equiv C$ triple bond is formed by one strong σ bond and two weak π-bonds. The bond energy of a $C\equiv C$ bond is 803.3 KJ mol^{-1} as compared to 598 KJ mol^{-1} for C=C bond in ethene and 347 KJ mol^{-1} for C-C bond in ethane.

→ Bond lengths :→

- The minimum distance between nuclei of two bonded atoms in known as bond length.
- This distance does not remain constant because of perpetual atomic vibrations.
- Thus the bond length is actually the average distance between the centers of nuclei of the two bonded atoms where the attractive and repulsive forces just balance each other and the potential energy is minimum.
- It is expressed either in Angstrom (A°) or Picometer (pm) units [$1 A° = 100 pm = 10^{-10} m$]
- The value of bond length between two atoms x and y remains constant and is independent of the nature of molecules in the same class of compounds.
- For example, the C–H bond distance, remains 110 pm in a large number of compounds like methane, ethane, propane.
- Various bond lengths have been measured by physical methods such as x-ray diffraction, electron diffraction and spectroscopic methods.
- some typical bond lengths are listed in table

Bond	Bond length (pm)	Bond	Bond length (pm)
H—H	74	C—Br	191
N—N	109.4	C—I	213
Cl—Cl	199	C—C	154
C—Cl	176	C=C	134
C—H	110	C≡C	119
C—N	147	H—F	92
C—O	143	H—Cl	127
C—S	182	H—Br	141
C—F	213	H—I	161

→ Factors affecting bond length:→

1. Size of the atom:→

- Bond length increases with an increase of size of the bonded atoms.

$C-F = 142\ pm$

$C-Cl = 177\ pm$

$C-Br = 191\ pm$

$C-I = 213\ pm$

2. Multiplicity of bonds:→

- Bond length decreases with an increase in the multiplicity of bonds (or bond order).

$C-C = 154\ pm$

$C=C = 134\ pm$

$C\equiv C = 120\ pm$

3. Type of hybridisation:→

- The size of hybrid orbitals decreases in the order: $sp^3 > sp^2 > sp$.
- As a larger orbital forms a longer bond, therefore, carbon-carbon bond length decreases in the order.

$$C-C\,(sp^3-sp^3) > C=C\,(sp^2-sp^2) > C\equiv C\,(sp-sp)$$

- Further, the order of electronegativity of hybrid orbitals is : $sp > sp^2 > sp^3$ i.e., the electronegativity of carbon is maximum in sp-hybridised state and minimum in sp^3-hybridised state.
- The bond formed with a more electronegative atom will be shorter than that formed with a less electronegative atom. Consequently, a C-H bond formed with a carbon orbital of high s-character will be shorter than the one formed with a carbon orbital of high p-character.

- The change in hybridisation of the atomic orbitals in carbon thus produces a change in the covalent atomic radius which decreases in passing from tetrahedral (sp^3) to diagonal (sp) type of hybridisation.
- In following table, average bond lengths depending upon the state of hybridisation of the bonded atoms, are listed.

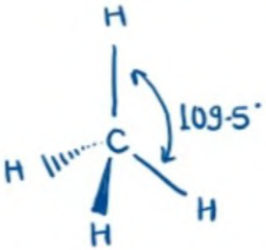
Bond type	Bond length (pm)	Typical compound
C—C		
sp^3-sp^3	154	CH_3-CH_3
sp^3-sp^2	150	$CH_3-CH=CH_2$
sp^3-sp	146	$CH_3-C\equiv CH$
sp^2-sp^2	148	$CH_2=CH-CH=CH_2$
sp^2-sp	143	$CH_2=CH-C\equiv CH$
sp-sp	138	$HC\equiv C-C\equiv CH$
C=C		
sp^2-sp^2	134	$CH_2=CH_2$
sp^2-sp	131	$CH_2=C=O$
sp-sp	128	$O=C=C=C=O$
C≡C		
sp-sp	120	$HC\equiv CH$
C—H		
sp^3-H	111	CH_4
sp^2-H	110	$CH_2=CH_2$
sp-H	108	$H-C\equiv C-H$

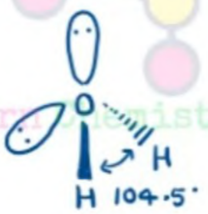
→ Bond angles :→

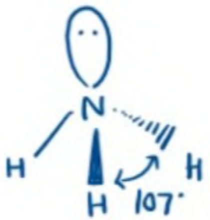
- A polyatomic molecule has more than one bonds which are formed by overlap of atomic or hybrid orbitals.
- Due to directional nature of the hybrid or atomic orbitals these bonds make angle between them.
- The angles between the line representing the two bonds are known as bond angles.
- Bond angles are measured by x-ray diffraction and spectroscopic methods.
- Because of constat atomic vibrations, the bond angles thus measured are really average bond angles.
- The shape of the molecules are dependent on the bond angles.

Example

CH_4, Methane, tetrahedral, H–C–H bond – 109.5°
H_2O, Water, V-shape, H–O–H bond – 104.5°
NH_3, Ammonia, Pyramidal, H–N–H bond – 107°







→ Factors affecting bond angles :→

1. Type of hybridisation :→

sp = 180°
sp^2 = 120°
sp^3 = 109.5°

✤ These angles may deviate from their regular geometry values due to some other electronic effects.

2. The number of lone pairs and bond pairs :→

- According to the VSEPR theory, the magnitude of repulsion between lone pairs and bond pairs decreases in the order :

$$l.p.-l.p. > l.p-b.p > b.p-b.p$$

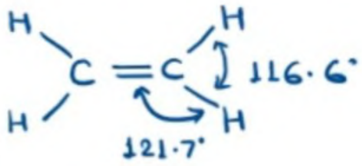
- The regular geometry distorts due to presence of lone pairs and bond angle decreases.

Example

Molecule →	CH_4	NH_3	H_2O
Hybridisation →	sp^3	sp^3	sp^3
No. of b.p. →	4	3	2
No. of l.p. →	0	1	2
Geometry →	Tetrahedral	Pyramidal	V-shape
Bond angle →	109.5°	107°	104.5°

- The bond angle also changes due to presence of π-electrons which repel other bond electrons.

Example:- change in bond angle for sp^2 carbon (120°) in case of ethylene.



Ethylene

→ Bond energy :→

- During the formation of a bond, certain amount of energy is released. The same amount of energy will be needed to break this bond.
- Bond energy may thus be defined as the energy required to break a bond between two atoms.
- It is expressed in units of kJ mol^{-1}.
- The values of bond energies for certain diatomic molecules are given in following table –

Bond	Energy (kJ mol^{-1})
H — H	435
N — N	297
Cl — Cl	247
Br — Br	192
F — F	155
I — I	150
O — O	146

- These values are called bond dissociation energies and are represented by D.
- However, for a polyatomic molecule containing more than one covalent bond, the term bond energy may have two different meanings –

(i) Bond dissociation energy (D) is the energy required to break one mole of a particular bond in the molecule.

(ii) Bond energy (E) is the average energy per bond, which is the average of the different bond dissociation energies for such bond present in the molecule.

→ Example: →

- When four hydrogen atoms of methane removed one by one, we get four different D values, Thus,

$$CH_4 \longrightarrow CH_3 + H \qquad D(CH_3\text{-}H) = 427 \text{ KJ mol}^{-1}$$

$$CH_3 \longrightarrow CH_2 + H \qquad D(CH_2\text{-}H) = 439 \text{ KJ mol}^{-1}$$

$$CH_2 \longrightarrow CH + H \qquad D(CH\text{-}H) = 452 \text{ KJ mol}^{-1}$$

$$CH \longrightarrow C + H \qquad D(C\text{-}H) = 347 \text{ KJ mol}^{-1}$$

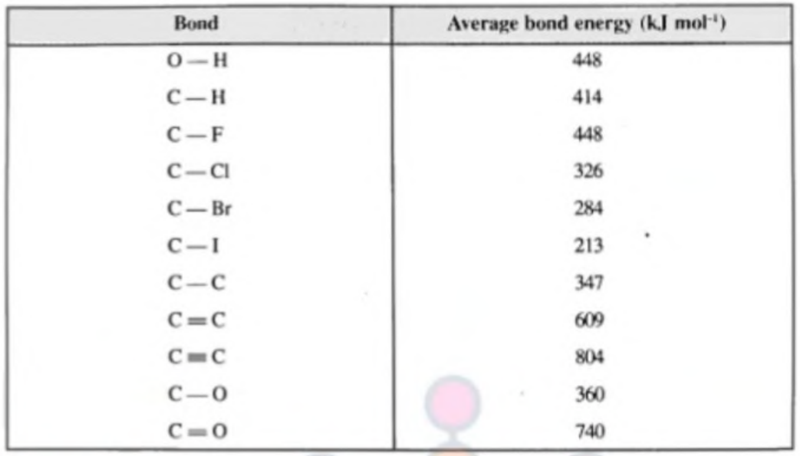
- All values of D are different because C-H bond dissociation energy not includes the energy needed for breaking of bond but it also includes the energy changes accompanying the rehybridisation at the carbon atom in each step.
- Direct atomisation of methane requires 1665 KJ mol^{-1}, which is the sum of all the four D values listed above.

$$CH_4 \longrightarrow C + 4H \qquad \Delta H = 1665 \text{ KJ mol}^{-1}$$

The bond energy per C-H bond in methane is thus fourth of this value, i.e.

$$\frac{1665}{4} = 416.25 \text{ mol}^{-1}$$

- Since, a diatomic molecule has only one bond, D is equal to E in such cases.
- Some bond energies obtained by taking the average from measurements on several polyatomic molecules are listed in following table.



Bond	Average bond energy (kJ mol^{-1})
O — H	448
C — H	414
C — F	448
C — Cl	326
C — Br	284
C — I	213
C — C	347
C = C	609
C ≡ C	804
C — O	360
C = O	740

→ Factors affecting Bond energies: →

1. Size of atom: →

$$\text{Bond energy} \propto \frac{1}{\text{Size of atom}}$$

Example:- C–F (448) > C–Cl (326) > C–Br (284) > C–I (213) KJ mol^{-1}

2. Bond length: →

$$\text{Bond energy} \propto \frac{1}{\text{Bond length}}$$

Example:- C≡C (804) > C=C (609) > C–C (347) KJ mol^{-1}

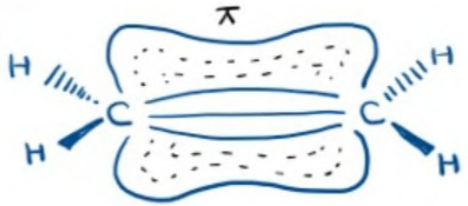
3. Type of hybridisation: →

- size of hybrid orbitals $sp^3 > sp^2 > sp$ – Electronegativity order $sp^3 < sp^2 < sp$
- Bond length order $sp^3 > sp^2 > sp$ – Bond energy order $sp^3 < sp^2 < sp$

Example:- For C–H bond → $C(sp^3)$–H (416) < $C(sp^2)$–H (443) < C (sp)–H (500) KJ mol^{-1}

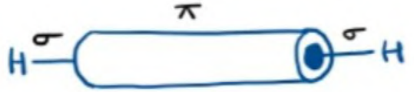
→ Localized and delocalized bonds:→

- Atomic or hybrid orbitals overlap to form covalent bonds where the electrons are either localized or delocalized.
- When the electrons forming a bond spend most of their time in the space between the two bonded atoms, they are called localized electrons and such a bond is called localized bond. e.g., all σ bonds are localized bond.
- When the electrons are moving in and out of space between two bonded atoms, they are called delocalized electrons and the bond formed by them is called delocalized bond.
- Electrons forming π - bonds may be either localized or delocalized.
- π bonds of ethylene is localized because the electrons forming π- bond ethylene are confined to the space between two carbon atoms in such a way that these electrons are distributed equally in the space above and below the plane of C-C, σ bond.



(A) Ethylene

- Two π- bonds of acetylene are delocalized because of electrons forming the π- bond in the plane of paper do not confined to the space above and below the plane of C-C, σ bond and similarly the electrons of other π- bond formed in perpendicular direction, do not confined to that space



(B) Acetylene

Actually, all these electrons merge together to form a cylindrical electron cloud around C-C, σ bond.

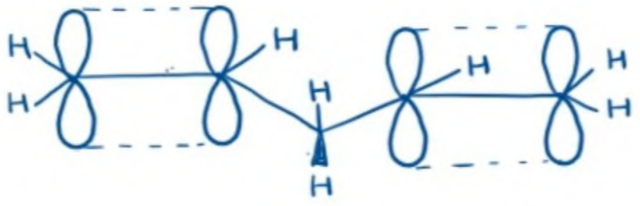
- Other examples are 1,3-butadiene and benzene where two or more than π-bonds are in conjugation. The electrons of one π-bond are delocalized into the space of other π-bond and vice versa. This delocalization occurs through the overlap of unhybrid p orbitals present on each sp^2 carbon.

(a) 1,3-butadiene:→

- All the four carbon atoms of 1,3-butadiene lie in the same plane due to which all the p-orbitals at four carbon atoms overlap with each other and π-electrons can move to a limited extent over all the four carbon atoms i.e., π-electrons of 1,3-butadine are delocalised.

1,3-Butadiene

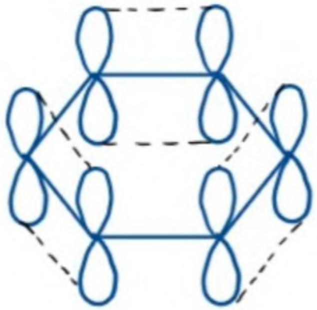
- In contrast, the π-electrons and hence the π-bonds are localized in isolated dienes such as 1,4-pentadiene, where each pair of π-electrons is confined to the space between two carbon atoms.

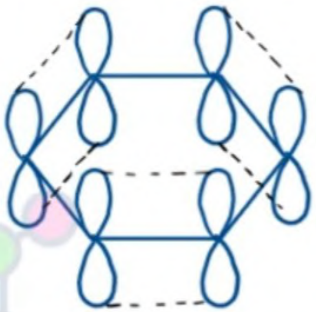


1,4-pentadiene

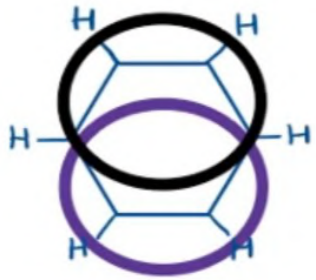
(b) Benzene: →

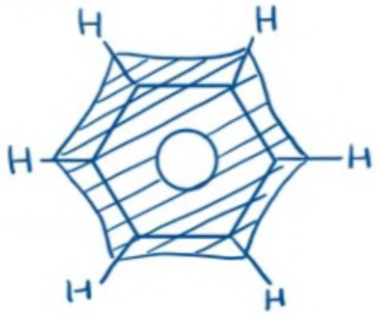
- In case of benzene there are six sp^2 hybridised carbon atoms and each sp^2- carbon has one unhybridised p-orbital containing one electron.
- These p-orbitals are so close to each other that they can overlap sideways to form π- bond.
- There were two modes for overlap of adjacent p-orbitals as shown in fig. -





- Actually, each p-orbital overlaps equally well with the p-orbitals on adjacent two carbon atoms on both side to form a doughnut shaped π- electron cloud above and below the plane of carbon and hydrogen atoms. i.e. these three π- bonds of benzene are delocalized.





→ Armit and Robinson Structure: →

- As the three π- bonds of benzene are completely delocalized, it is not proper to represent benzene with a hexagonal ring with three double bonds at alternate positions since the positions of π- bonds is not fixed. Therefore, benzene is written as shown in fig. This representation was given by Armit and Robinson.

→ Inclusion compounds and clatherates:→

- Certain organic solids such as urea, thiourea, hydroquinone, etc. have crystalline shapes.
- However, in some cases, the crystalline shapes of these compounds undergo a change in presence of certain other compounds.
- The former compounds whose crystalline structures change are called hosts while the latter ones in whose presence the crystalline structures of the former changes are called guests.
- The crystal lattice of host compounds forming long channels or cage like structures has enough space to trap the guest molecules.
- There is no chemical bonding between the host and the guest molecules. There are only weak van der Waals forces of attraction which hold the guest molecule in the space provided by the host molecules.

→ Types of Host - Guest Addition compounds:→

- These compounds are divided in to two types on the basis of space available within the crystal lattice of host compounds.

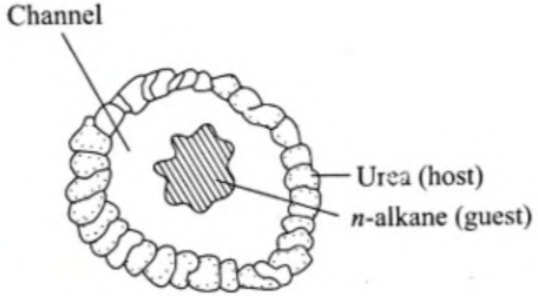
1. Inclusion compounds:→

- The host-guest addition compounds are known as inclusion compounds when the space available within the crystal lattice of the host molecule in the form of long channels.

(a) Urea as host:→

- Ordinarily urea crystallizes in tetragonal shape.
- However, when a guest is present, Urea crystallizes in the hexagonal lattice trapping the guest molecules (n-alkane) in the space.
- This compound is stable due to van der Waals attraction between host and guest.

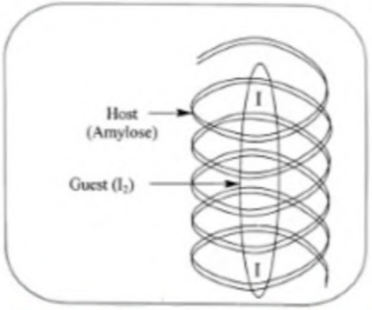
- The diameter of the urea channel is about 500pm and the type of guest molecules will depend upon their shape and size only.
  Example:- Dipropyl fumarate is a guest but dipropyl maleate is not.



(b) Thiourea as host :→

- n-alkanes cannot act as guest for thiourea. However, 2-bromooctane, cyclohexane, chloroform etc. trapped in the channels of thiourea.

(c) Amylose as host :→



- Starch gives deep blue colour with iodine.
- Starch is a mixture of amylose (water soluble) and amylopectin (water insoluble).
- Amylose has helical structure which easily accommodate an iodine molecule.
- Thus the blue colour is due to formation of an inclusion complex between amylose and iodine.

→ Use of inclusion compounds :→

- These compounds are useful in separating certain isomers that would be otherwise difficult to separate.
  For example:- n-octane can be separated from its branched chain isomers, because only n-octane can for inclusion compound with urea.
- Urea inclusion compounds used to resolving racemic mixtures.
  For example :- (±) racemic mixture of 2-chlorooctane forms two different inclusion compounds (diastereomeric) which can be separated by fractional crystallization.

2. Clatherates:→

- The host-guest addition compounds are known as clatherates, when the space available within the crystal lattice of the host molecule in the form of cage.
- The adducts in which the host molecule has cage like cavities are clatherates or cage compounds.
- Unlike inclusion compounds, the crystal lattice of clatherates is not fully occupied by the guest.
- On the basis of nature of host, clatherates are divided in two categories-

(a) Quinol clatherates:→

- Quinol clatherates have hydroquinone as host.
- In these complexes, three molecules of hydroquinone which are held by hydrogen bonding form a cage containing several cavities of 400 pm diameter.
- The guests are methanol, SO_2, CO_2, H_2S, CH_3CN and noble gases such as Ar, Kr, Xe, etc.
- clatherates have some vacant space in the cage structures because all cavities are not filled.

(b) Water clatherates:→

- Six molecules of water form the cage like structure.
- The guests are Cl_2, propane, CH_3I and noble gases such as Ar, Kr, Xe etc.
- When water is frozen under high pressure of any one of the above noble gas, solid crystalline compounds of the formula H_2O: gas (5.75 : 1) are obtained. These clatherates are called as noble gas hydrates. These are preserved at low temperature because at room temperature they decompose whereby trapped gases are released.

→ Use:→

- He and Ne can be separated from other noble gases because He & Ne do not form clatherates.
- Radioactive isotopes of Kr and Xe can be stored as clatherates.

→ Charge transfer complexes :→

- When an electron rich compound (called the donor molecule and designated as D) is mixed with an electron poor or deficient compound (called the acceptor molecule and designated as A) in 1:1 ratio, it forms a complex called charge transfer complex
- In the formation of charge transfer complexes, the donor molecule may donate either a non-bonding (or an unshared) pair of electron or a pair of electrons of π- system (an olefinic double bond or the aromatic ring system) to acceptor molecule. The former donor is called an n-donor and the latter is called as a π- donor.
- Such complexes are also known as electron- donor- acceptor complexes or EDA complexes.
- The formation of a charge transfer complex may be represented as –

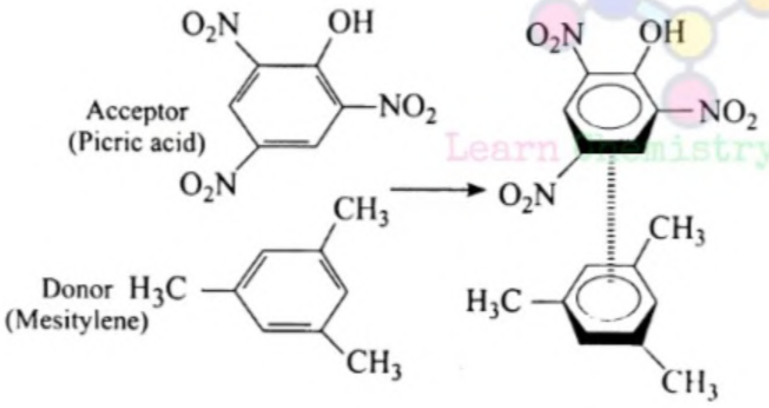
$$\underset{\text{Donor}}{D} + \underset{\text{Acceptor}}{A} \longrightarrow \underset{\text{Charge transfer complex}}{[D\text{---}A]} \longleftrightarrow D^{+}\text{—}A^{-}$$

- In these complexes, the bonding force between donor and the acceptor molecules are the weak coloumbic forces.
- A bonding of such type which results from attractive forces between donor and acceptor molecules is called charge transfer interaction.

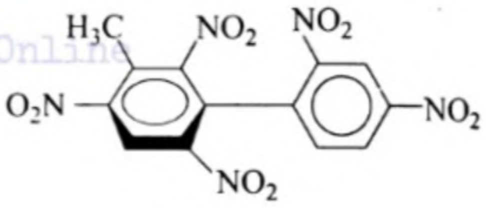
→ Example:→

- Picrates are the most common example of charge transfer complexes.
- Picrates are formed by the reaction of 2,4,6- trinitrophenol (picric acid) and aromatic hydrocarbon such as naphthalene, anthracene, mesitylene, etc.

- Picrates are yellow, orange or red coloured solids having definite melting point and hence are oftenly used as derivaties for characterisation of different compounds.
- Not only picric acid but other polynitro aromatic compounds such as 1,3,5- trinitrobenzene, for similar addition compounds.
- The formation of charge transfer complex is faciliated by the presence of electron donating substituents in D and electron- withdrawing substituents in A.
- Donor has a low ionization potential and acceptor has a high electron affinity with low energy vacant orbital.
- Due to parallel arrangement of the two rings, overlap occurs between molecular orbitals of D and A (HOMO- LUMO) causing electron transfer.
- In absence of coplanarity, charge tranfer complex cannot formed.



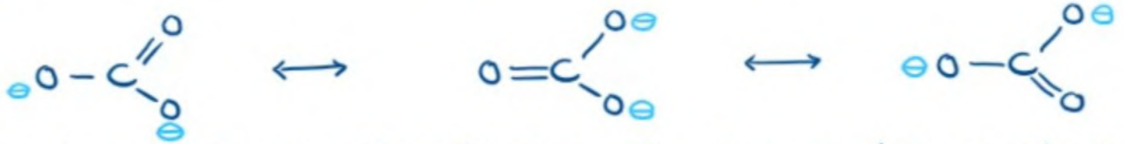
(Picrate)
(π-complex)



(Z)

→ Resonance :-

- There are a number of compounds for which it is possible to write more than one Lewis structures.
- However, none of these structures conforms to all the observed properties of these substances.
- For example, following three Lewis structures can be written for the carbonate anion.



- On the basis of all above three structures, it cannot be predicted that all C–O bonds are of equal length (130 pm). All structures have two C–O single bonds and one C=O double bond.
- The concept of resonance was introduced to explain such limitations of the classical Lewis structures.
- According to the theory of resonance or mesomerism for a molecule two or more Lewis structures (called resonance structures) can be written which differ only in the position of electrons but not in relative positions of atoms.

  The actual structure of the molecule is not represented by anyone of the resonance structure but is considered to be hybrid of all these structures.

  In other words, the actual molecule is considered to be a hybrid or mesomer (Greek b/w the parts) of all the possible Lewis structures which are referred as contributing or canonical forms.
- One of the important assumptions of this theory is that the contributing or cannonical forms have no real existance.
- Situation of resonance is represented using a double headed arrow (↔) which is placed between each pair of contributing forms.
- Double headed arrow does not signify the oscillation of molecule from Lewis structure to another.

- In fact, the word resonance does not mean the mixing of formal structures and, therefor, a less confusing term for this phenomenon π- electron delocalization has been coined.
- An important example of resonance is that of benzene, which can be considered to be hybrid of two Kekulé forms, and three Dewar forms with the latter contributing only little.
- The real structure of benzene molecule cannot be represented by any of these formulations, as all the carbon- carbon lengths are equal (139 pm). This value is somewhat intermediate between Carbon - carbon single bond (154 pm) and carbon - carbon double bond (134 pm). Further, benzene resist addition reactions and is a highly unsaturated compound.


Kekulé forms


Dewar forms

→ Rules for resonance method:→

– The following rules for the use of resonance method enable us to predict when and to what extent resonance is important in determining the properties of various molecules.

(i) Structures contributing towards the hybrid must conform to real Lewis structures, i.e., there can be no structure with penta-covalent carbon and bi-covalent hydrogen.

(ii) Resonance involves movement of only π and n-electrons and a resonance structure can be derived from another by a series of one or more short electron shift without changing the relative position of atoms. In other words, if two or more double bonds or a double bond and an unshared pair of electrons are in conjugation, there is delocalization of π or n-electrons.

(iii) All resonance structures must have same number of paired electrons. Thus $\dot{C}H_2-\dot{C}H_2$ does not contribute towards resonance of ethylene.

(iv) All resonance structures do not contribute equally to the hybrid. It is expected that structures with more covalent bonds are more stable than those with fewer. Because each bonds increases the stability.

(v) When atoms of different electronegativities are involved, the structure which places a negative charge on the most electronegative atom would be more important.

(vi) Resonance contribution is the greatest when there are two or more equivalent contributing forms of lowest energy.

(vii) If there is only a single contributing structure of lowest energy, the resonance hybrid possesses properties expected for that structure.

(viii) In order to achieve maximum overlap of p-orbitals, which is necessary for delocalization, it is essential that the skeleton should be planar in conjugated system.

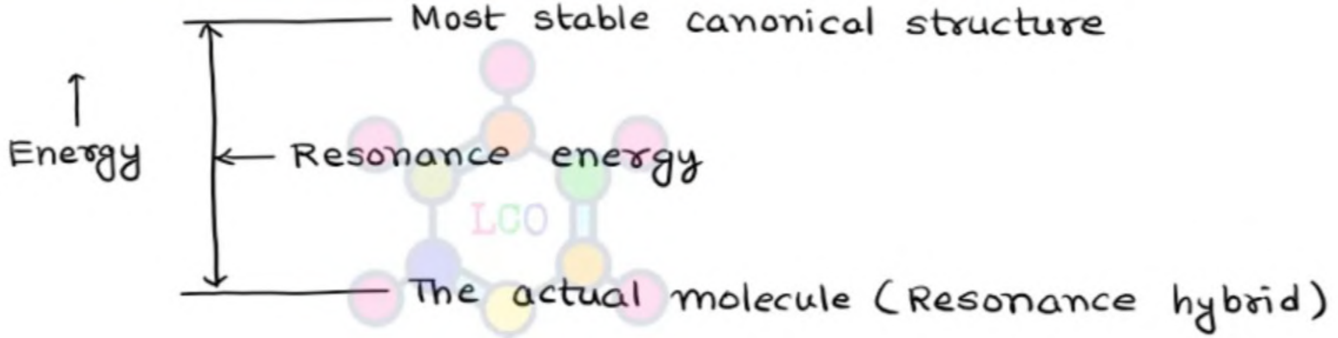
(ix) Resonance structures involving charge separation are less stable than non-polar structures.

(x) Resonance structures having like charges on adjacent atoms are of high energy and hence unimportant.

(xi) structures with greater number of covalent bonds contribute more towards the resonance hybrid.

→ Resonance energy:→

- A resonance hybrid (or actual molecule) is always more stable than any of its contributing forms. This stability is due to delocalisation of electrons and is measured in terms of resonance energy.
- It may be defined as the difference between the actual energy of a molecule and the energy calculated for the most stable of resonating structure.



→ Calculation:→

1. From heat of hydrogenation:→

- The resonance energy of benzene has been calculated by comparing heats of hydrogenation of benzene with those of cyclohexene and 1,3-cyclohexadiene.

$\Delta H = -232.6$ KJ mol^{-1} (nearby double of cyclohexene)

- On the basis of these values one would expect that the heat of hydrogenation for kekule structure of benzene to be $-119.6 \times 3 = 358.8$ KJ mol^{-1}. But the experimental value of the heat of hydrogenation of benzene has found to be -208.36 KJ mol^{-1}.

$\Delta H = -208.36$ KJ mol^{-1}

- Thus, the molecule of benzene is stabilised by $358.8 - 208.36 = 150.44$ KJ mol^{-1}. This difference is referred to as resonance energy.

2. From heat of formation:→

- Heat of formation of Kekule structure of benzene (ΔH_f) can be calculated from various bond dissociation energies.

$$\Delta H_f = 6(\text{Bond energy of C–H bond}) + 3(\text{Bond energy of C–C bond}) + 3(\text{Bond energy of C=C bond})$$

$$= 6 \times 414 + 3 \times 347 + 3 \times 609$$

$$= 5352 \text{ KJ mol}^{-1}$$

- The experimental value is 5503.8. Hence, the resonance energy of benzene is

$$5503.8 - 5352 = 151.8 \text{ KJ mol}^{-1}$$

→ Characteristics of resonance hybrid :→

1. Stability :→

- A resonance hybrid (or actual molecule) is always more stable than any of its contributing forms.
- This stability is due to delocalisation of electrons and measured in terms of resonance energy.
- No. of equivalent resonance structure ∝ delocalisation of electrons ∝ resonance energy ∝ stability.

Example :-

- Both benzene and 1,3- butadiene have conjugated double bonds but the resonance energy of benzene (151 KJ mol^{-1}) is larger than that of 1,3 - butadiene (12·5 KJ mol^{-1}). Consequently, benzene is more stable than 1,3 - butadiene.

2. Bond length :→

- The bond lengths in the resonance hybrid (or actual molecule) differ from those in the respective contributing structures.

Example:-

- All the C–C bond lengths in benzene are 139 pm while each of the two contributing Kekule's structures has two types of carbon-carbon bond lengths (C-C → 154 pm and C=C → 134 pm).

→ Inductive effect :→

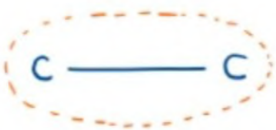
- When a covalent bond is formed between two atoms having different electronegativities, there is induced a permanent dipole in such a bond. This induction of due to polarisation is reffered to as the inductive effect.
- This polarisation is due to drift of the shared pair of electrons towards the more electronegative atom resulting in the origin of small fractional charges on the constituent atoms (δ^+ and δ^-).

$-\overset{|}{\underset{|}{C}}-H$ or $-\overset{|}{\underset{|}{C}}:H$ symmetrical sharing of bonded electron pair (no significant difference in electronegativities of bonded atoms)

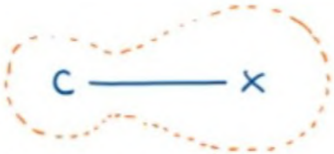
$-\overset{|}{\underset{|}{C}}-C$ or $-\overset{|}{\underset{|}{C}}:C$ symmetrical sharing of bonded electron pair (same type of atoms)

- When the carbon atom of alkane is attached to a more electronegative atom or group (x), the electron pair of covalent bond shift slightly towards x resulting in distortion of molecular orbital. Consequently, the atom or group (x) acquires a partial negative charge (δ^-) and the carbon a partial positive charge (δ^+). Thus

$-\overset{|}{\underset{|}{C}}-x$ or $-\overset{|\,\delta^+}{\underset{|}{C}}:x^{\delta^-}$ unsymmetrical sharing of bonded electron pair - origin of fractional charges due to higher electronegativity of x



Electron density evenly
distributed (non-polar)



Electron density unevenly
distributed (polar)

- The inductive effect is represented by an arrow with its head in the middle of covalent bond pointing in the direction of electron displacement.

$$\overset{\delta^+}{C_3} \rightarrow \overset{\delta^+}{C_2} \twoheadrightarrow \overset{\delta^+}{C_1} \ggg \overset{\delta^-}{X}$$

- This induction travels along the chain through the bonds. The extent of this effect, however, diminishes with increase in distance.
- This type of σ - electron shift along a saturated chain of atoms due to presence of polar covalent bond is called inductive effect or I-effect. Sometimes it is also called transmission effect or T-effect.

→ Characteristics of inductive effect:→

- I-effect involves only the tendency of displacement of σ-electrons and it occurs in polar single covalent bonds.
- It is a permanent effect and cannot be reversed.
- This effect decreases progressively with an increasing distance between cabon atom and the other atom or group causing this effect.

- The electrons are shifted slightly without leaving their orbitals, i.e., only little distortion of the orbitals occurs which leads to polarisation.
- Different atoms or groups cause polarisation of covalent bond to different extent depending upon their power of accepting or donating the electrons.

→ Types of inductive effect:→

- The inductive effect is designated as +I or -I effect depending upon whether the atom or group is electron repelling (donor group) or electron withdrawing (acceptor group), respectively.
- For example, chlorine shows -I effect whereas methyl group shows +I effect.
- The inductive effect is permanent effect involving polarisation of a covalent bond.

$C \rightarrow Cl$ $\qquad$ $C \leftarrow CH_3$

-I effect $\qquad$ +I effect

→ Group showing -I effect:→

- $-C_6H_5$, $-OH$, $-OCH_3$, $-I$, $-Br$, $-F$, $-COOH$, $-CN$, $-NO_2$ etc.
- The -I effect of the groups having hetero atoms such as oxygen, nitrogen halogen, etc., is due to the greater electronegativity of these groups as compared to carbon.
- These groups thus cause -I effect due to their electron attracting nature.

→ Group showing +I effect:→

- $-CH_3$, $-CH_2-CH_3$, $-CH(CH_3)_2$, $-COO^-$ etc.
- The +I effect of these groups is due to electron donating nature of alkyl groups.
- The more highly substituted the alkyl group, stronger is its +I effect.

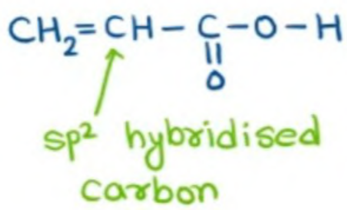
Tert-butyl > Isopropyl > n-propyl > Ethyl > Methyl > Hydrogen.

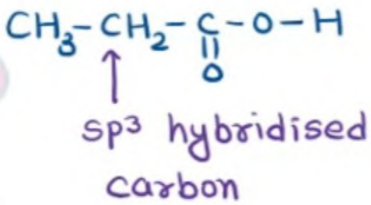
This order of +I effect can be explained on the basis of hyperconjugation.

→ Inductive effect and Hybridisation:→

- Inductive effect also depends on the state of hybridisation of the atom linked by a covalent bond.
- For example:-

Acrylic acid ($CH_2=CHCOOH$) is stronger acid than propionic acid (CH_3CH_2COOH).
It may be due to the electron-withdrawing effect (-I) of the sp^2-hybridised carbon atom next to carbonyl group although the resonance effect of α,β-unsaturated carbonyl system would tend to decrease the acid strength.


$CH_2=CH-\overset{\displaystyle O}{\overset{\|}{C}}-O-H$

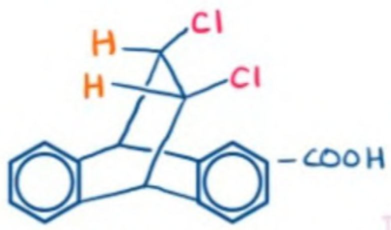

$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-H$


$CH_2=CH-\overset{\displaystyle O}{\overset{\|}{C}}-O-H \longleftrightarrow \overset{\oplus}{C}H_2-CH=\overset{\displaystyle O^{\ominus}}{\overset{|}{C}}-O-H$

- Further, the acid strength of propiolic acid ($CH\equiv C-COOH$) is many times as much as that of propionic acid because of strong electron-withdrawing effect (-I) of sp-hybridised carbon atom next to carbonyl group.

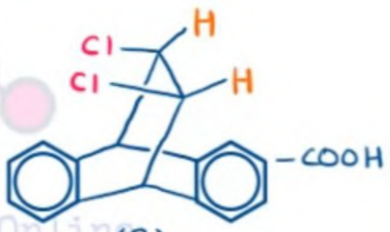
→ Field effect:→

- Inductive effect operates through bonds. However, there is another effect operating not through the bonds but through space or solvent molecules. This effect is called field effect.
- Field effect depends upon the geometry of molecule whereas inductive effect depends upon the nature of bonds.
- For example, in isomers A and B, the inductive effect of the chlorine atoms on the –COOH group must be same since the same number of bonds intervene. Hence, acid strength of the two acids (A and B) should be same. Actually, the acid strength of the two acids has been found to be different.



(A)

pKa = 5·67 (stronger acid)



(B)

pKa = 6·07 (Weaker acid)

→Reason:→ The acid strength is different due to field effects. The chlorine atoms are closer in space to the –COOH group in isomer A than they are in isomer B. This example shows that sometimes field effects are even more pronounced than inductive effects.

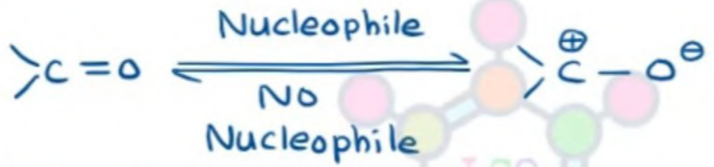
Therefore, the chlorine atoms in A, being closer to the acid group as compared to B, will exert greater electron-withdrawing effect in A as compared to B. Hence, the isomer A is a stronger acid than B. This is also supported by the pKa values of the two acids.

→ Electromeric effect:→

— The transfer of π- electrons of a multiple bond to one of its bonded atoms in presence of an attacking reagent is called the electromeric effect and is designated as E-effect.

— Exomple:-

The nucleophilic addition of cyanide ion to a carbonyl group. The π- electrons of C=O bond are completely transferred to more electronegative oxygen atom. However, the molecule will revert back to its original electronic state when the attacking reagent is removed. Thus this is a temporary effect.



The net result of the above displacement is generation of positive charge on the carbon atom which facilitates the attack of the nucleophile on it.

→ Types:→

1. Electron-donating electromeric effect or +E effect:→

— When π- electrons of the double bond are transferred to the atom to which attacking reagent get finally attached, the effect is called +E-effect.

Example:- Addition of electrophiles to alkenes.

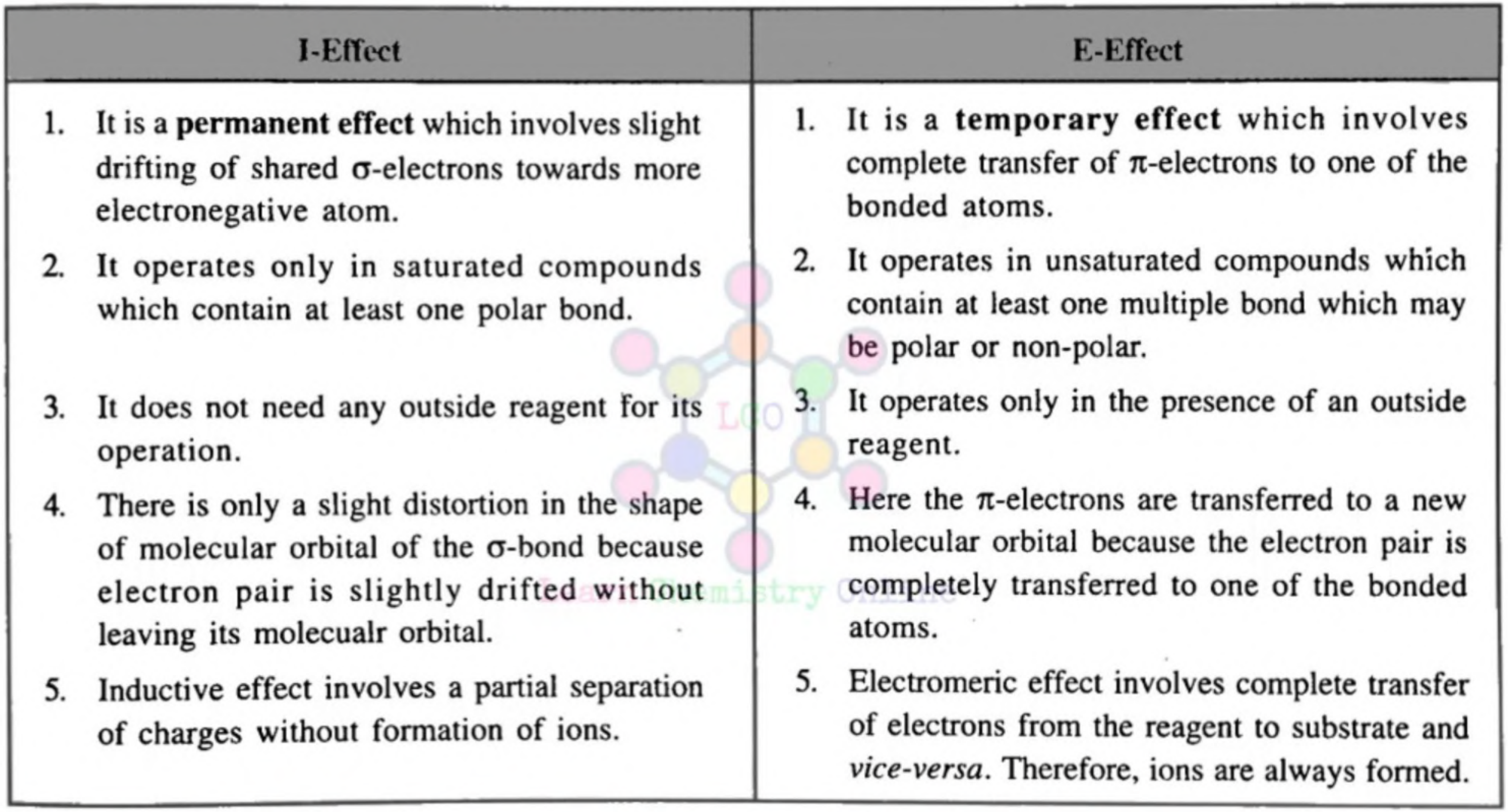
(+E - effect)

2. Electron-withdrawing electromeric effect or −E effect :→

- When π- electrons of the double bond are transferred to the atom to which attacking reagent does not get attached, the effect is called −E-effect.

Example:- The addition of nucleophile to the carbonyl group.

→ Comparison of I-effect and E-effect :→



I-Effect	E-Effect
1. It is a **permanent effect** which involves slight drifting of shared σ-electrons towards more electronegative atom.	1. It is a **temporary effect** which involves complete transfer of π-electrons to one of the bonded atoms.
2. It operates only in saturated compounds which contain at least one polar bond.	2. It operates in unsaturated compounds which contain at least one multiple bond which may be polar or non-polar.
3. It does not need any outside reagent for its operation.	3. It operates only in the presence of an outside reagent.
4. There is only a slight distortion in the shape of molecular orbital of the σ-bond because electron pair is slightly drifted without leaving its molecualr orbital.	4. Here the π-electrons are transferred to a new molecular orbital because the electron pair is completely transferred to one of the bonded atoms.
5. Inductive effect involves a partial separation of charges without formation of ions.	5. Electromeric effect involves complete transfer of electrons from the reagent to substrate and *vice-versa*. Therefore, ions are always formed.

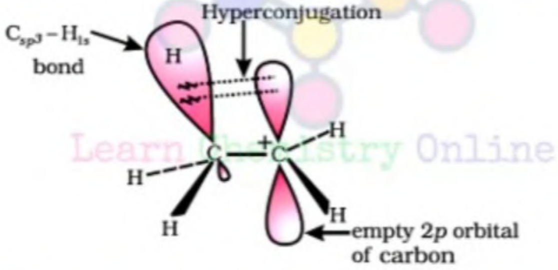
- In certain molecules both I- and E- effects operates together. In some cases they may reinforce each other whereas in others they may oppose each other. In case they oppose each other, the E- effect always dominates over the I-effect.

→ Hyperconjugation: →

- Hyperconjugation is a general stabilising interaction.
- It involves delocalisation of σ electrons of C-H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p-orbitals.
- The σ electrons of C-H bond of the alkyl group enter into partial conjugation with attached unsaturated system or with the unshared p-orbital.
- Hyperconjugation is a permanent effect.

- Example: →

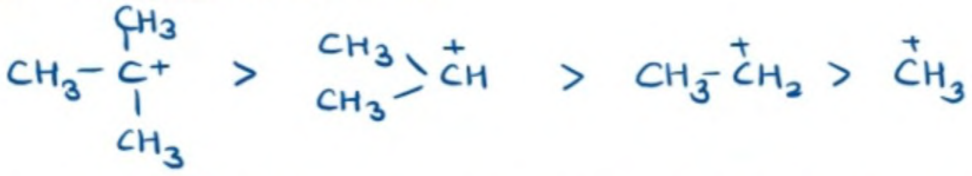
- In case of ethyl cation ($CH_3\overset{+}{C}H_2$), the positively charged carbon atom has an empty p orbital. One of the C-H bonds of methyl group can align in the plane of this empty p-orbital and the electrons of C-H bonds in plane with this p-orbital can be delocalised into the empty p-orbital.



- This type of overlap stabilises the carbocation because the electron density from the adjacent σ bond help in dispersing the positive charge

$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}^{+} \longleftrightarrow H-\underset{H}{\overset{H^{+}}{C}}=\underset{H}{\overset{H}{C}} \longleftrightarrow H^{+}\ \underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \longleftrightarrow H-\underset{H^{+}}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}$$

- In general, greater the number of alkyl group attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation.
- Relative stability of carbocations is



$$(CH_3)_3C^+ > (CH_3)_2\overset{+}{C}H > CH_3-\overset{+}{C}H_2 > \overset{+}{C}H_3$$

- Hyperconjugation is also possible in alkenes and alkylarenes.
- Hyperconjugation is also called no bond resonance or Baker-Nathan effect.

→ Importance of hyperconjugation effect :→

- Stability of carbocations and free radicals.
- Stability of alkenes.
- Directive influence of alkyl groups.
- Shortening of carbon-carbon bonds adjacent to unsaturated bond.