

# Structure and Bonding

## # Introduction :-

More than a Century ago all substances then known were classified on the basis of source from which they were derived. The Compounds which were of mineral origin were known as Inorganic and those of vegetable or Animal origin were called organic.

e.g. table salt, marble,  $\text{CO}_2$  were inorganic whereas acetic acid (from vinegar), alcohol (from wine), tartaric acid (from grapes), citric acid (from lemons) and sucrose (from sugarcane) were organic.

It was assumed that organic Compounds could be produced only by living matter, for living matter was thought to possess a 'vital force'. "vital force theory."

In 1850 the vital force theory was finally and decisively disproved. It had become evident, however that most of the Compounds formed by living cells (Plants and Animals) contained Carbon. Hence the emphasis was shifted from origin to composition and organic Compounds came to be considered as those containing Carbon.

"Organic Chemistry" is defined as the study of Carbon Compounds. However there are several exceptions, e.g. Carbon monoxide  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{KCN}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , Thiocyanates  $\text{NaSCN}$ ,  $\text{KSCN}$  (cyanates), Carbides  $\text{CaC}_2$ . These Compounds are studied as part of Inorganic Chemistry because of their Properties.

# Why organic chemistry is a separate discipline?

Due to following reasons they are studied separately.

### 1) Large Number of Compounds

There are approximately 10,000 known inorganic Compounds and this number is not rapidly increasing. On the other hand there are over 5 million known organic Compounds and several thousand new Compounds are synthesised each year.

## # Localized chemical bond :-

Localized chemical bonding may be defined as bonding in which the electrons are shared by two and only two nuclei.

e.g. Covalent bond between two hydrogen atoms of  $H_2$  molecule. there is greatest possibility of finding electrons in the region between the two nuclei.

Concentration of negatively charged electrons between the two positive nuclei that holds the nuclei together. since spins of the two electrons are antiparallel, this produces less repulsion between two electrons, tending to concentrate them in the internuclear region. The net result is that the electron density for paired  $e^-$ s is greatest between the two nuclei. Such a bond is said to be Localized bond.

Due to this bond or This localization of electron pair in a chemical bond gives rise the properties of bond lengths, dipole moment, force constants etc.

## # Orbital hybridisation. : Geometry and shape of molecules. :-

The electronic Config. of carbon is,

$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$ . according to valence bond theory.

Carbon appears to be divalent.

Similarly,  $Be_4$   $1s^2, 2s^2$  appears to be inert.

$B_5$   $1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$ . should be monovalent.

but beryllium is divalent in  $BeF_2$ , Boron is trivalent in  $BF_3$  and Carbon is tetravalent in  $CH_4$ .

In order to explain the geometry of molecules a new concept called as orbital hybridization was introduced.



## Hydrogen bond :-

It has been found that hydrogen possess a special ability to form a link between two electronegative atoms. one link is in the form of polar covalent bond with one electronegative atom and another link is in the form of electrostatic attraction with another electronegative atom. (represented by dotted line).

Due to uneven sharing of electrons,  $\delta^+$  charge develops on hydrogen atom which attracts negative end of a group of the same or other molecules forming a weak bond. This type of bond i.e. weak bond formed due to dipole-dipole attraction is called a hydrogen bond.

Due to electrostatic character, hydrogen bond is much weaker (bond energy 3-10 kcal/mole) than a covalent bond (bond energy 50-100 kcal/mole).

Generally hydrogen bonds formed with Oxygen, Nitrogen and fluorine.

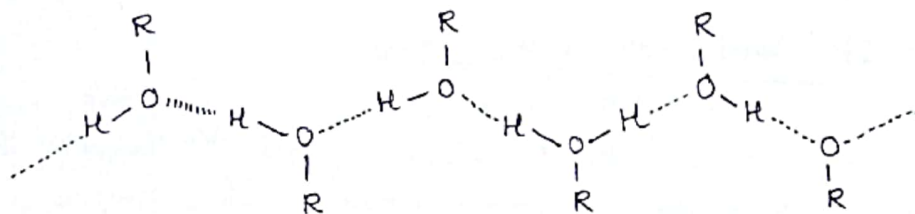
There are two types of hydrogen bonding

### 1) Intermolecular hydrogen bonding :- (diff. molecule).

This type of bonding exists in alcohols, Carboxylic acids, amines, HF and other Org. Compounds.

Due to difference in electronegativity  $\delta^+$  &  $\delta^-$  charges are developed on  $\overset{\delta^-}{O} - \overset{\delta^+}{H}$ .

Positively charged hydrogen attracts -ve oxygen atom of another alcohol molecule forming a hydrogen bond.



Intermolecular hydrogen bond.

More energy is required to break the intermolecular hydrogen bond. Due to these type of bonding the m.p. and B.P. of organic compounds increases.

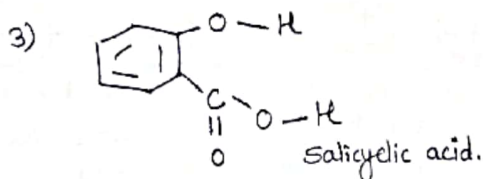
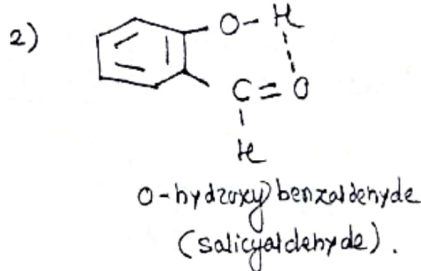
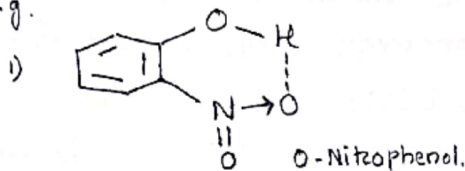
Solubility of these types of substances in  $H_2O$  is only due to ability of forming a hydrogen bond with water. Thus alcohols are soluble in water but Alkane, alkene and alkynes having less EN difference between Carbon & hydrogen atom i.e. not possess polar groups & hence do not form intermolecular hydrogen bonding with  $H_2O$ . Hence alcohols are more soluble in water than hydrocarbons.

2) Intramolecular hydrogen bonding :- (same molecule).

In this type bonding occurs within two atoms of the same molecule. This type of hydrogen bonding is also called as 'Chelation'.

This type of hydrogen bonding is only possible when two groups are present at ortho positions in the same molecule.

e.g.



Due to formation of intramolecular hydrogen bonding there is no possibility of intermolecular hydrogen bonding & thus prevents molecular association which rises m.p. & B.P.

Hence due to intramolecular hydrogen bonding M.P. and B.P. decreases.

e.g. M.P. of o-nitrophenol is  $44^\circ C$  while m.p. of p-nitrophenol is  $114^\circ C$ .

Intramolecular hydrogen bonding decreases solubility of organic compounds in water due to chelation which prevents hydrogen bonding between the water & compound.

### ✓ 3) Charge Transfer Complexes :-

Reaction of two compounds results in a product that contains all the mass of two compounds, the product is called as "Addition Compound". In these type of formation one molecule acts as donor (D) and donates an unshared pair or pair of electrons in a  $\pi$  orbital of a double bond or aromatic system. Another molecule, capable of accepting electron acts as acceptor (A). When the two molecules combine due to attractive forces, a bond results between donor and acceptor molecule. Such a interaction is termed as electron-donor-acceptor or charge transfer interaction and formed compound is called as electron-donor-acceptor (EDA) complex or charge transfer complex.

The formation of EDA or charge transfer complex is facilitated by presence of  $e^-$  donating substituents in 'D' and  $e^-$  withdrawing substituents in 'A' molecule.

Distance between D & A is about  $3-3.5 \text{ \AA}$ .

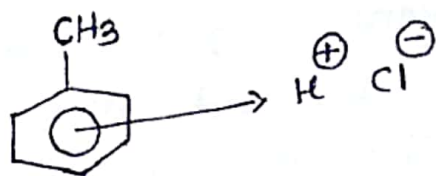
Which is larger than normal covalent bond length. Charge transfer complex shows dipole moment which indicates the charge separation in ground state of EDA complex.

#### Examples.

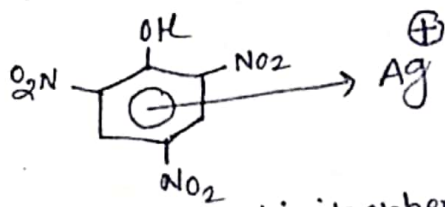
1) Toluene forms charge transfer complex with HCl at  $-78^\circ\text{C}$ . Here benzene with  $\pi e^-$  cloud acts as 'D' &  $\text{H}^+$  forms HCl as 'A'.

$2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$   
 $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$   
 $\text{Cu} + \text{H}_2\text{O} \rightarrow \text{Cu(OH)}_2$   
 $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$   
 $\text{Mg} + \text{HCl} \rightarrow \text{MgCl}_2$



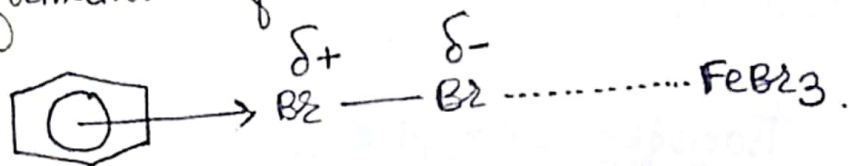


2) Aromatic hydrocarbons also form charge transfer complexes with halogens.



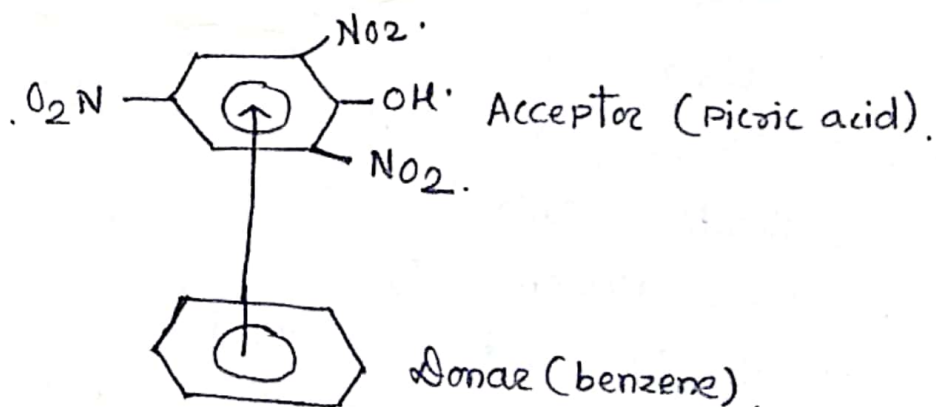
2,4,6 trinitrophenol. (Picric acid).

3) Benzene in the presence of Lewis acid like  $FeBr_3$  reacts with  $Br_2$  to form bromobenzene. Mechanism shows there is formation of EDA complex.



4) Picric acid forms stable coloured crystalline charge transfer complexes. Called as Picrates. Generally with aromatic hydrocarbons. (Naphthalene, Anthracene).

in the formation of complex, bonding is possible because both benzene rings and of donor and acceptor lies in parallel planes.

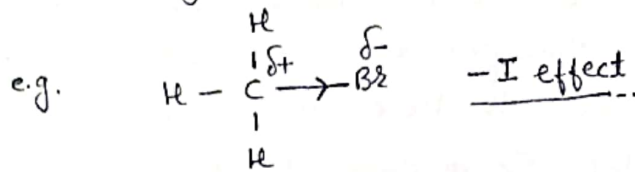


4) Inclusion

# 1) Inductive and field effect :-

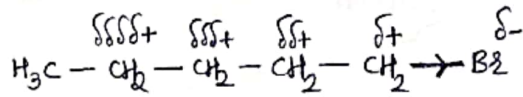
Covalent bond between two atoms differs in their electronegativities. Thus e<sup>-</sup>s are shifted towards more electronegative atom. as a result  $\delta^+$  &  $\delta^-$  charges observed.

Permanent displacement of e<sup>-</sup>s in a sigma ( $\sigma$ ) bond due to the presence of electronegative atom or group and formation of partial polar molecule is called as Inductive effect denoted by I & represented by  $\rightarrow$ , arrowhead pointing towards more EN atom.

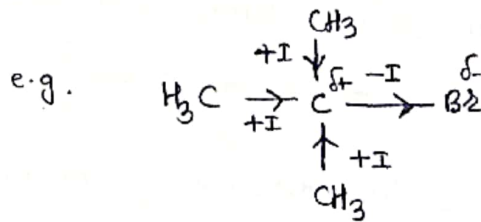


It is a permanent effect & always transmitted along a chain of carbon atoms, but it decreases as the distance from the EN atom increases.

Generally I effect diminishes beyond carbon atom number four.



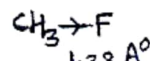
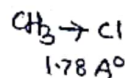
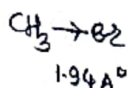
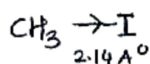
electron releasing (repelling) groups like  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $(\text{CH}_3)_2\text{CH}$ ,  $\text{OCH}_3$  etc. are said to exhibit +I effect and electron attracting (withdrawing) groups like  $-\text{NO}_2$ , halogens,  $\text{CHO}$ ,  $\text{C}=\text{O}$  etc are said to exhibit -I effect.

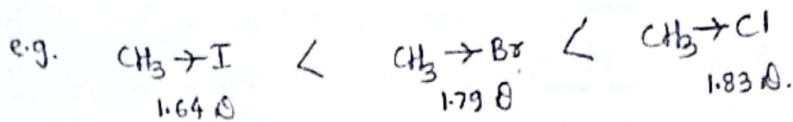


## 2) Applications of Inductive effect :-

### 1) Effect on bond length :-

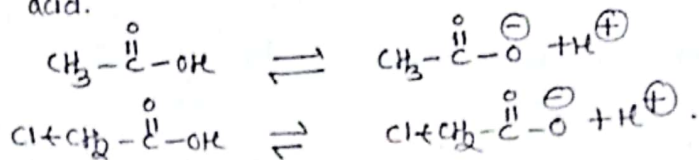
Inductive effect produces ionic character in the bond. The bond length of covalent bond decreases with increase in inductive effect due to presence of more EN atom or group. e.g.



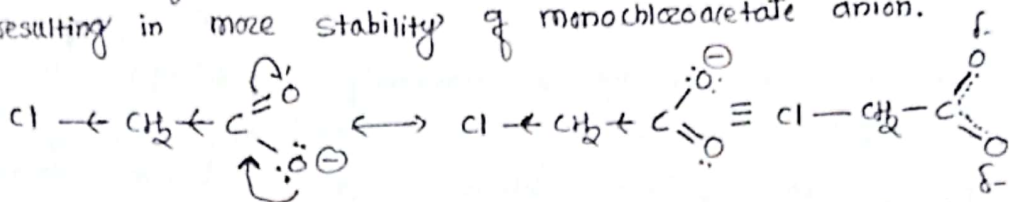


3) Strength of Carboxylic acids :-

Case I. Electronegative Substituent particularly attached to the  $\alpha$ -Carbon atom of Carboxylic acid, increases the acidity of Carboxylic acids. (-I effect).  
e.g. ① Monochloroacetic acid is 100 times more acidic than acetic acid.

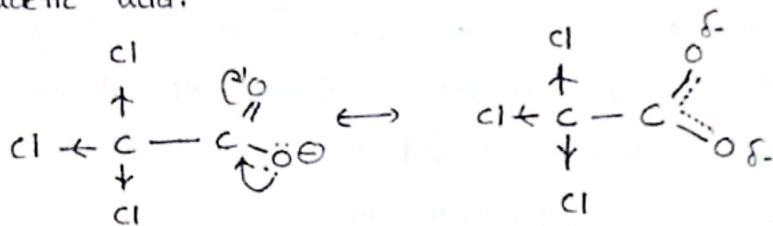


Due to inductive effect of EN chlorine atom, electrons on oxygen atom of chloro acetate anion are more delocalized resulting in more stability of monochloroacetate anion.



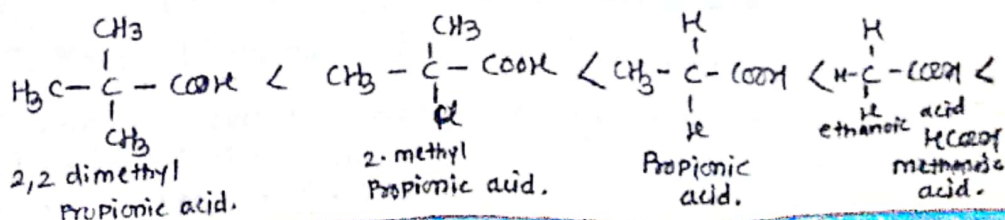
but in case of acetic acid, due to +I of  $\text{CH}_3$  gr. electrons on oxygen of acetate anion are less delocalized resulting in less stability of acetate anion. Hence less acidic than monochloroacetic acid.

② Trichloroacetic acid is 7000 times more acidic than acetic acid.



Case II. The presence of greater number of alkyl groups on  $\alpha$ -Carbon atom of a Carboxylic acid decrease the acidity of Carboxylic acid. (+I effect) Due to +I effect destabilize the corresponding Carboxylate anion resulting less ionization of Carboxylic acid in the solution.

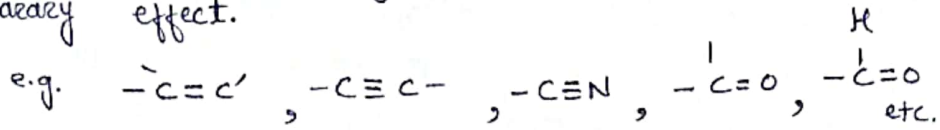
e.g. Increasing order of acidity of alkyl substituted acetic acid can be represented as,



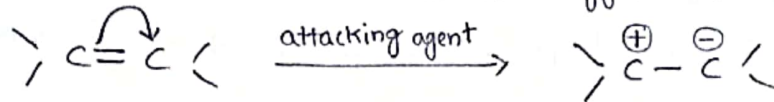


2) Electromeric effect :-

This type of effect observed in org. comp. which having double or triple bonds. It is temporary effect.

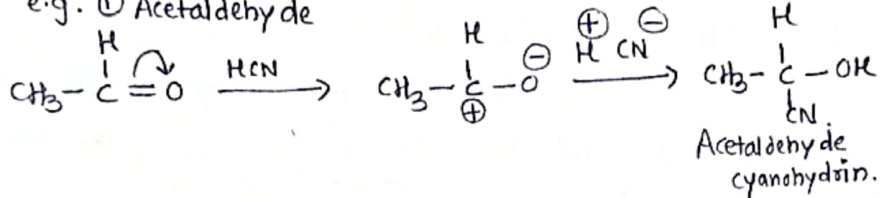


In this effect if presence of attacking reagent either electrophile or nucleophile, one electron pair in  $\pi$  bond completely shifted to another atom & give polar molecule it termed as electromeric effect. (E)

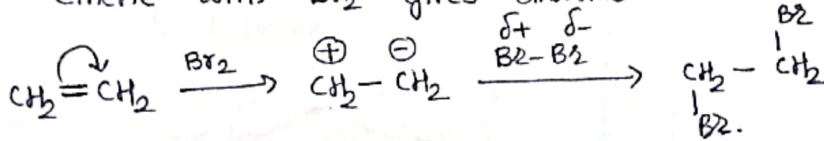


If this species with attacking reagent like HCN gives resp. compound.

e.g. ① Acetaldehyde



② ethene with  $Br_2$  gives dibromoethane.



3) Resonance effect (Mesomeric or Conjugative effect) :-

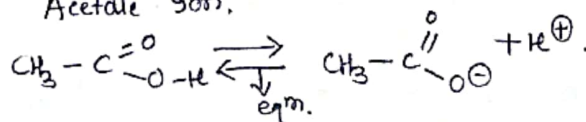
Properties of a compound cannot explained by a single Lewis structure. Two or more structure assigned to the compound which differ in the arrangement of e's of  $\pi$  bond or lone pair of e's but none of them represents true (Real) structure of a molecule. These hypothetical structures are called as resonating or canonical structures.

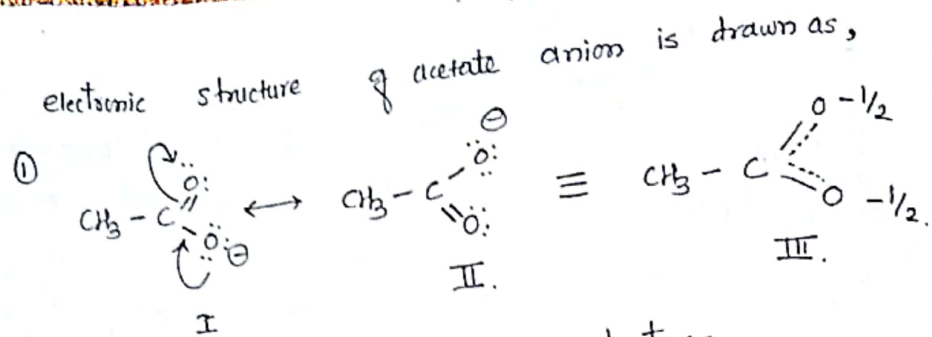
Phenomenon is known as resonance & effect called as resonance or mesomeric or conjugative effect.

It is permanent effect.

Resonance hybrid structure is more stable than other canonical structures. It is denoted by double headed arrow ( $\longleftrightarrow$ ).

e.g. Acetate ion.



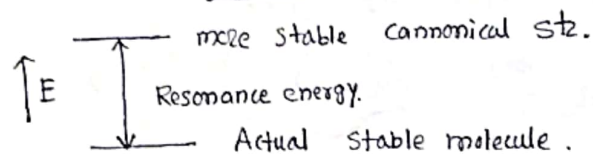


Str. I & II are Canonical structures.

Str. I or str. II are not real structures of acetate anion. Its true structure is not adequately represented by any single Lewis structure. Hence real str. represented by non-conventional Lewis structure III. called as Resonance hybrid.

In str. III a negative charge is delocalized over both of the oxygen atoms. Curved arrow  $\curvearrowright$  are used to show electron delocalization.

The difference in energy between the actual molecule and the Canonical form of the lowest energy is called as resonance energy.

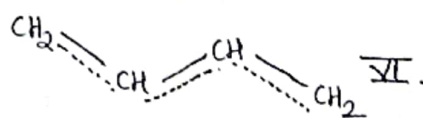
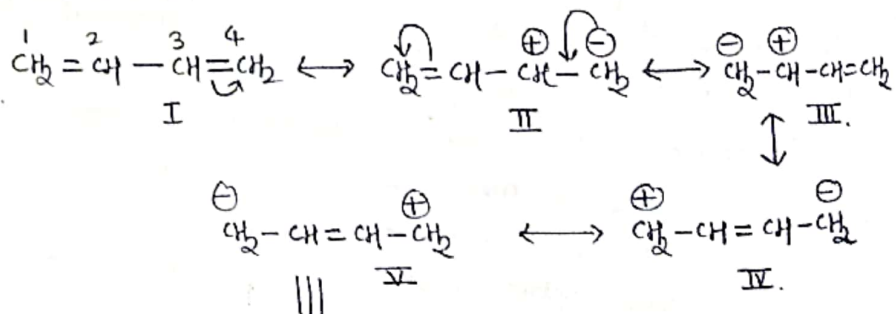


② In benzene (Kekule's 'Resonating' structures.)



Resonance hybrid structure.

③ 1,3 Butadiene.



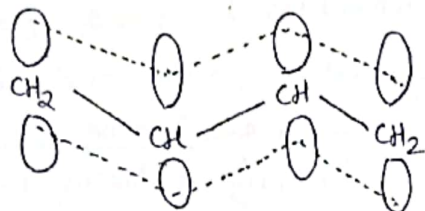
In 1,3 Butadiene C=C bond lengths bet<sup>n</sup> C<sub>1</sub>-C<sub>2</sub> & C<sub>3</sub>-C<sub>4</sub> are found to be longer than alkene which indicates that these double bonds have some single bond character.

Similarly, single bond bet<sup>n</sup> C<sub>2</sub>-C<sub>3</sub> is found to be slightly shorter than alkane this indicates that C<sub>2</sub>-C<sub>3</sub> bond has some double bond character.

Canonical form of 1,3 butadiene is shown in VI which is formed due to sidewise overlapping between four P<sub>z</sub> orbitals of four sp<sup>2</sup> hybridised carbon atoms. It results in delocalization, i.e. spreading of four p<sub>z</sub> electrons over four carbon atom in the form of π e<sup>-</sup> cloud above and below the plane of molecule.

This type of equal spreading of e<sup>-</sup>s over the entire molecule creating π overlap & π bonding is called as 'delocalized bonding'.

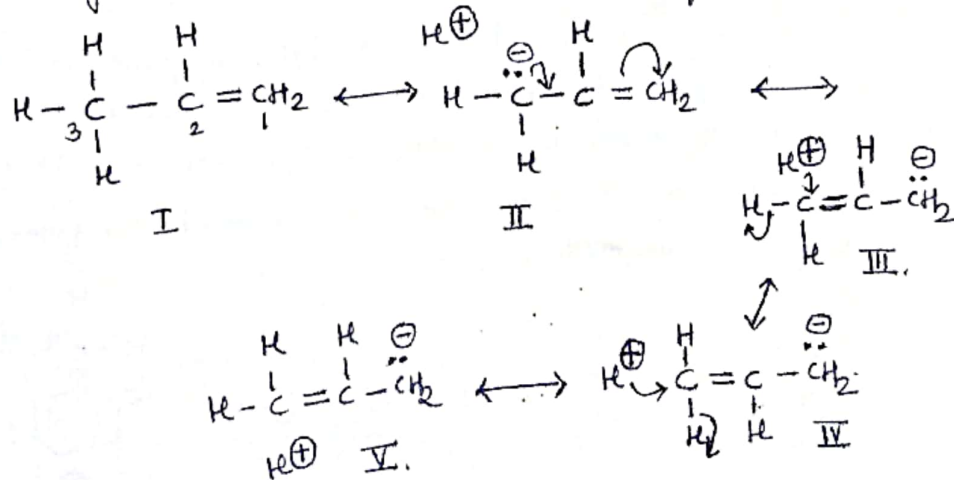
Due to delocalization C-C bond remains intermediate between localized single bonds (alkanes) and localized double bond (alkenes.)



#### 4) Hyperconjugation :-

There are certain organic molecules which are stabilized due to conjugation involving 6 electrons. This type of extended conjugation involving 6 bond orbitals (e<sup>-</sup>s of 6 bond), generally of C-H or C-X bond (X = halogens) is called as hyperconjugation.

e.g. 1-Propene Resonance hybrid of Propene are,





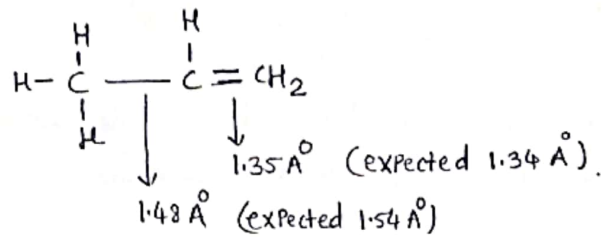
In structures II, III, IV and V resonating structures, there is no covalent bond between carbon and hydrogen atoms.

These structures possess less number of covalent bonds than the main uncharged I form.

Hence this type of hyperconjugation is also called as no bond resonance and resonating structures are called as hyperconjugative structures.

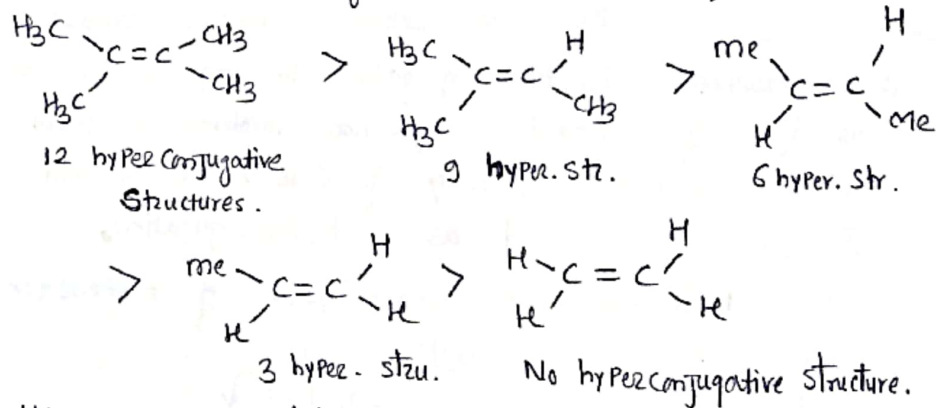
Due to this effect ionic character of C-H bond and partial delocalization of its e<sup>-</sup>s increases. Hyperconjugation decreases the bond length.

e.g. In Propene.



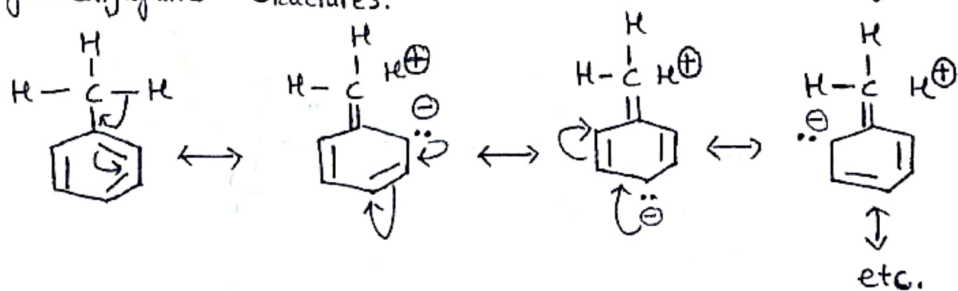
More number of resonating structures gives more stability to the molecule. Hence Propene is more stable than ethene. Stability of alkene increased by attachment of more number of alkyl groups to the double bonded carbon atom.

e.g. stability order of some alkenes are,



In this series tetramethyl ethylene is most stable due to four CH<sub>3</sub> groups i.e. 12 equivalent hyperconjugative structures.

# Stability of Toluene can be explained by following hyperconjugative structures.



## 5) Steric effect :-

Influence of inductive or hyperconjugative effects on the electron availability within the molecule may be modified by operation of steric factor.

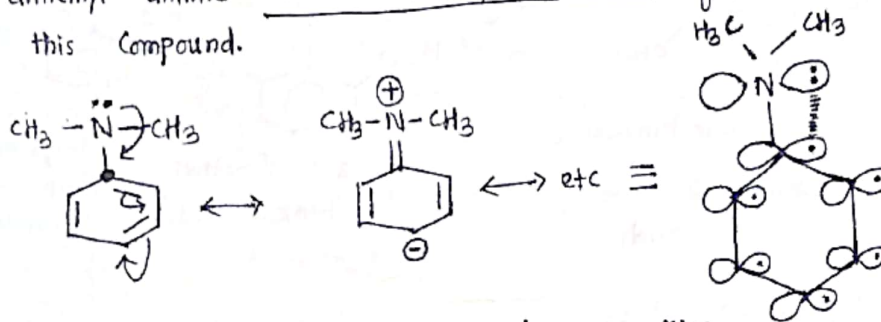
Due to this effect effective delocalization of  $\pi$  e<sup>-</sup>s, and approach of reagent to reacting centre is disturbed due to presence of bulky groups on reacting groups of molecule.

e.g.

① Nitrogen atom of N,N dimethyl aniline and 2,6 dimethyl N,N dimethyl aniline possess lone pair of electrons.

In N,N dimethyl aniline lone pair of e<sup>-</sup>s on Nitrogen gets delocalised over benzene ring due to coplanarity bet<sup>n</sup> p<sub>z</sub> orbital of Nitrogen atom containing lone pair of e<sup>-</sup>s and p<sub>z</sub> orbital of benzene ring.

Hence lone pair of e<sup>-</sup>s on Nitrogen atom of N,N dimethyl aniline is not readily available for the basicity of this compound.



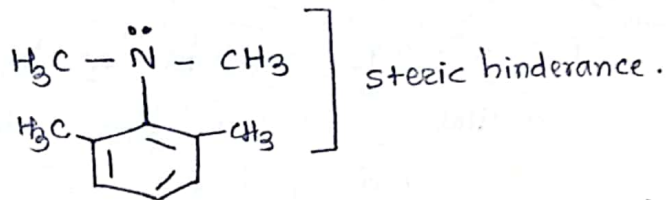
effective delocalization in N,N dimethyl aniline.

In 2,6 dimethyl N,N dimethyl aniline, due to presence of two bulky CH<sub>3</sub> groups at 2,6 positions (at ortho-position with respect to (CH<sub>3</sub>)<sub>2</sub>N group, as a result of steric hindrance, p<sub>z</sub> orbital of N atom containing lone pair of e<sup>-</sup>s and p<sub>z</sub> orbital of benzene ring are prevented from becoming parallel to each other & sidewise overlapping is inhibited. thus coplanarity for effective delocalization is disturbed.

ie lone pair of e<sup>-</sup>s on N atom does not get delocalized over benzene & thus remains available on Nitrogen atom to increase the basic strength.

Hence due to steric effect,

2,6 dimethyl N,N dimethyl aniline is more basic than N,N dimethyl aniline.

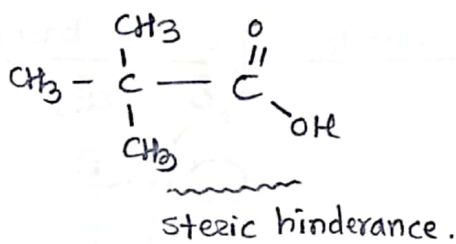


No coplanarity, Hence no effective delocalization in 2,6 dimethyl N,N - dimethyl aniline.

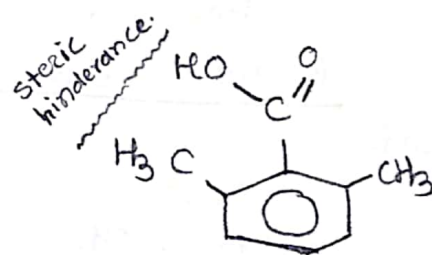
e.g. (2)

2,2 dimethyl propanoic acid and 2,6 dimethyl benzoic acid are not readily esterified due to carbonyl group in both compounds is sterically hindered by adjacent two bulky  $\text{CH}_3$  groups.

but 2,6 dimethyl phenyl acetic acid is readily esterified because -COOH group is beyond steric hinderance due to  $-\text{CH}_2$  group between them.



2,2 dimethyl propanoic acid.



2,6 dimethyl benzoic acid.

