

Lesson Structure

- 1.0 Objective**
- 1.1 Introduction**
- 1.2 Delocalised chemical bonding.**
- 1.3 Conjugation**
- 1.4 Cross Conjugation**
- 1.5 Resonance**
- 1.6 Hyperconjugation**
- 1.7 Tautomerism**
- 1.8 Aromaticity or Aromatic Character**
- 1.9 Annulenes**
- 1.10 Alternant and Non-Alternant Hydrocarbon**
- 1.11 Huckel Molecular Orbital Theory**
- 1.12 Solved Examples**
- 1.13 Model Questions**
- 1.14 References**

1.0 Objective

Objective of this unit is study the nature of bonding in organic compound. Aromaticity of benenoid, non benenoid compound and antiaromaticity on the basis of Huckel rule.

1.1 Introduction

When two half filled atomic orbitals belonging to two same or different atoms are brought near to each other, they overlap and form a new orbital called molecular orbital. It

surrounds both the nuclei and contains both the electrons. the schrodinger equation can be solved exactly only for one electron system such as hydrogen atom.

If it would be solved exactly for molecules containing two or more electrons, we would have a precise picture of the shape of the orbitals available to each electron and the energy for each orbital. Since exact solutions are not available drastic approximation must be made.

1.2 Delocalised Chemical Bonding :

Delocalised chemical bonding may be defined as bonding in which the electrons are shared by more than two nuclei.

1.3 Conjugation

A given atom or group is said to be in conjugation with an unsaturated system if

- (i) It is directly linked to one of the atom of the multiple bond through a single bond.
- (ii) It has π bond, positive charge, negative charge, odd electron or lone pair electron.

Example :-

1. $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
2. $\text{CH}_2 = \text{CH} - \overset{+}{\text{C}}\text{H}_2$
3. $\text{CH}_2 = \text{CH} - \overset{\cdot}{\text{N}}\text{H}_2$

Conjugation Positions of the molecule.

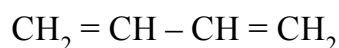
Alternate positions of the molecule having π bond, positive charge, negative charge, odd electron or lone pair of electron or lone pair of electrons are between as conjugate positions.

Example :-

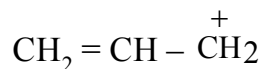
1. $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$
2. $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \overset{\cdot}{\text{C}}\text{H}_2 \text{CH}_3$
3. $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \overset{\cdot}{\text{N}}\text{H}_2$

Types of Conjugation :

- (1) **π, π conjugation** : If all conjugate positions have π bonds, then conjugation is known as π, π conjugation.



- (2) **Positive charge, π conjugation** : If this case, all conjugate positions have π bonds and only one conjugate position has positive charge. If this is the case then conjugation is known as positive charge, π conjugation.



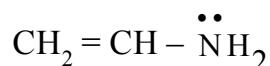
- (3) **Negative charge, π conjugation** : If the conjugate positions have π bonds and one conjugate positions has negative charge, then conjugation is known as negative charge, π conjugation.



- (4) **Odd electron, π conjugation** : If all conjugate positions have π bonds and only one conjugate position has odd electron, then conjugation is known as odd electron, π conjugation.

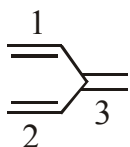


- (5) **Lone pair, π conjugation** : If all conjugate positions have π bonds and only one conjugate positions has lone pair then conjugation is known as lone pair, π conjugation.

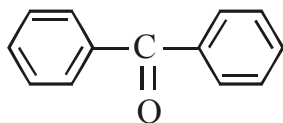


1.4 Cross Conjugation

In cross conjugated compounds, three groups are present, two of which are not conjugated with each other, although each is conjugated with the third. Examples are :



(1)



(2)



(3)

In example (1) 1 and 2 are not conjugated but third one is conjugated with 1 as well as 2. Cross conjugated trienes are known as dendralenes.

In example (2) carbonyl group is in conjugation to both the rings, but both rings are not in conjugation to each other.

In example (3) lone pair present on nitrogen is in conjugation to both double bonds but both double bonds are not in conjugation to each other.

1.5 Resonance

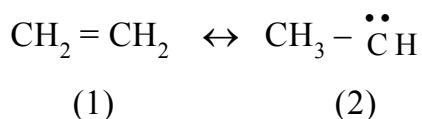
Resonance is a hypothetical state of a chemical species in which its electronic structure can be hypothetically represented by two or more resonating structures, each differing in the distribution of electrons.

Arguments based on resonance theory are usually made in a qualitative way.

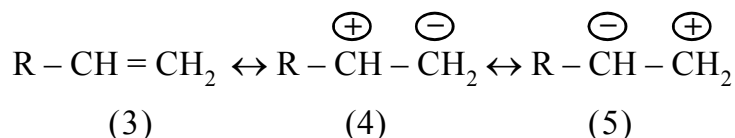
The elements of resonance theory that are necessary for qualitative applications are as follows :-

- (1) All the canonical structures must be written according to the Lewis method showing bonds, lone pair of electrons and formal charges, where required.
- (2) The positions of the atomic nuclei of the chemical species must remain unchanged in all the resonating structures.

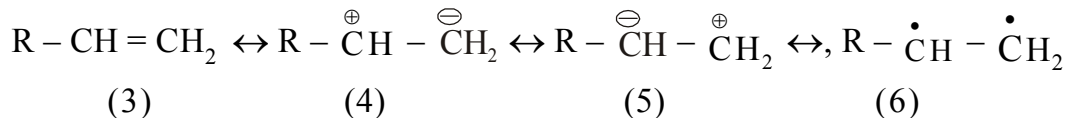
Thus (1) and (2) are not canonical structures.



- (3) To write resonating structures, only the π bonds can be converted to a lone pair of electrons and vice-versa. Thus, the resonance hybrid of alkene may be written as.



- (4) The number of unpaired electrons in each of the structures must be the same. Thus, structure (6) cannot be a resonating structures of the alkene.



- (5) The several resonating structures must be of comparable energies; this for alkenes, structure (4) and (5) have such a high energy in comparison to (3) that they do not at all contribute to the hybrid.
- (6) All atoms involved in the resonance must lie in the same planes or nearly in the same plane any change in structure which prevents planarity will diminish resonance simply because maximum overlap of p-orbitals can not be possible them to form π bond.

1.6 Hyperconjugation : Interaction between σ - Π or σ - p system

The delocalisation of σ -electrons through conjugation with Π -electrons (or with vacant or half filled p-orbital) is known as hyperconjugation. (or Baker-Nathan effect or no bond resonance).

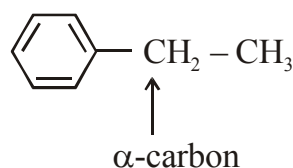
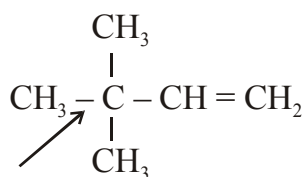
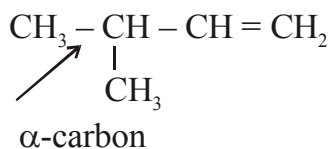
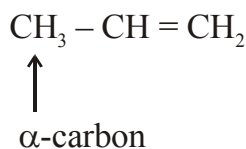
Structural Requirements of Hyperconjugation :

Any organic species can show hyperconjugation phenomenon if it will fulfil following conditions.

- (1) Compound should have sp^2 hybrid carbons of alkene, arene, carbocation or free radical.
- (2) α -carbon with respect to sp^2 hybrid carbon should have at least one hydrogen and hybridisation of α -carbon is sp^3 .

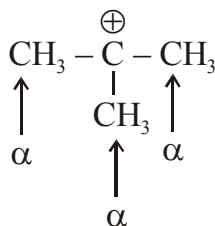
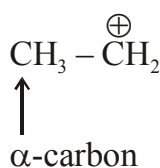
Thus hyperconjugation is of three types :

- (i) **$\sigma(C-H)$, π conjugation** : This type of conjugation occurs in alkenes and alkyl substituted aromatic compounds.

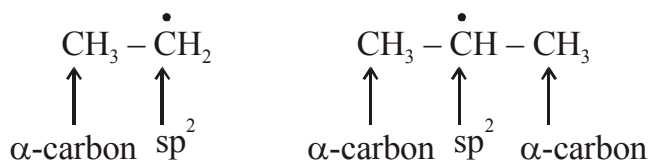


no hydrogen on α -carbon, no hyper conjugation

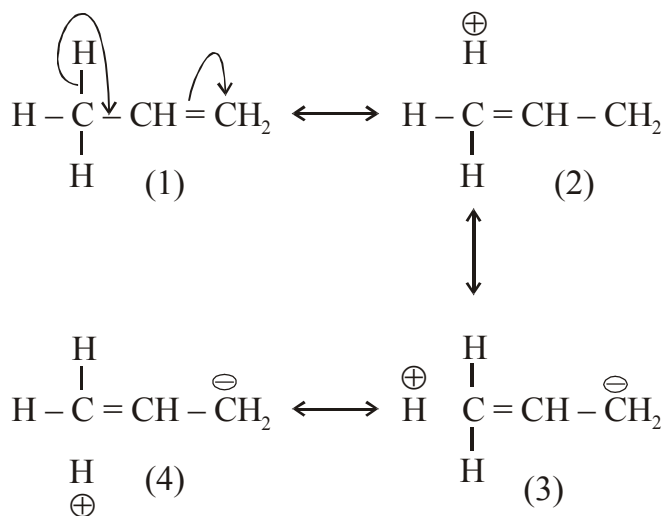
- (ii) **$\sigma(C-H)$, positive charge (vacant p-orbital) Conjugation** : This type of conjugation occurs in alkyl carbocations.



- (iii) **$\sigma(C-H)$, odd electron (incomplete-p-orbital) conjugation** : This type of conjugation occurs in alkyl free radicals.



Resonating structures due to hyperconjugation may be written involving “no-bond” between alpha carbon and hydrogen present on α -carbon.

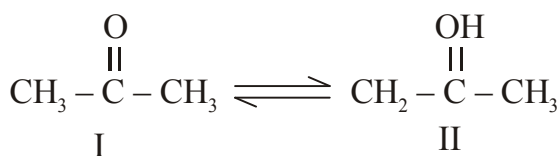


From the above resonating structures one can very easily conclude the following rules.

Number of resonating structures = Number of α -hydrogen + 1

1.7 Tautomerism

Tautomerism is the phenomenon in which two structural isomers differing in the relative positions of their atoms are spontaneously interconvertible and can exist in dynamic equilibrium. The two forms in tautomeric equilibrium are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds.



(I) and (II) are tautomers.

Classification of Tautomerism :

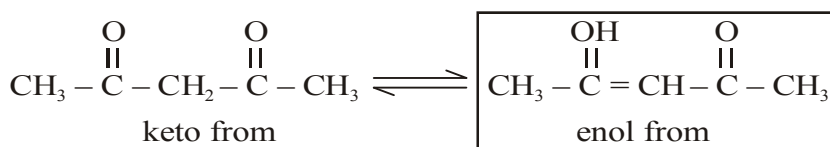
It is possible to classify all the compounds exhibiting tautomerism under three headings:

1. Open system of tautomerism or ionotropy.

2. Ring chain tautomerism.
3. Valence tautomerism.

Open-system of tautomerism :

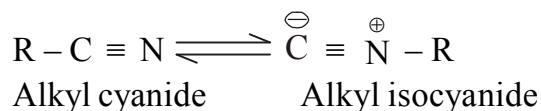
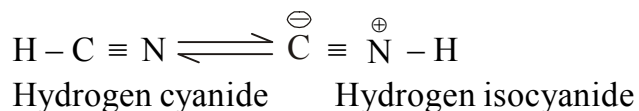
In this type of tautomerism, both tautomers are open chain compounds. In this type of tautomerism, tautomerisation takes place due to migration of acidic hydrogen in the form of a proton. Due to the migration of a proton, tautomerism is called prototropy. The classical example of prototropy is the keto-enol tautomerism.



Types of open system of Tautomerism :

It is possible to classify tautomerism (generally prototropy) into the following types on the basis of the number of atoms which are involved during the change.

1. **Diad system :** In this system the hydrogen or the group migrates from atom number-1 to atom number-2. The most common example of diad system is tautomerism between cyanides and isocyanides.

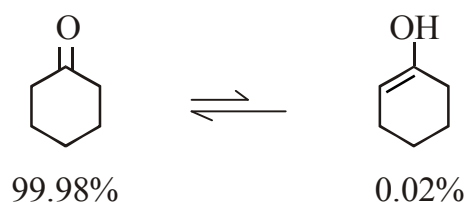
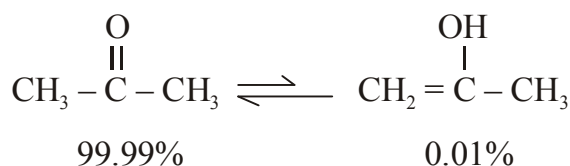


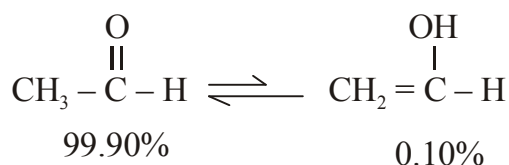
2. **Triad system :** In this system the acidic hydrogen migrates from atom number-1 to atom number-3. The most common example of triad system is keto-enol system.

Keto-enol system :

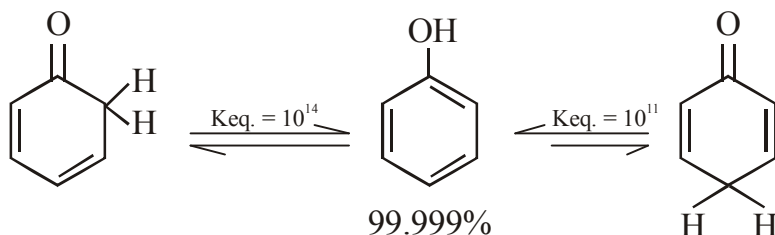
In a solution containing a trace of acid or base, a ketone or an aldehyde exists as an equilibrium mixture of its isomeric keto and enol forms.

For example ketones and aldehydes, the ketoform predominates.



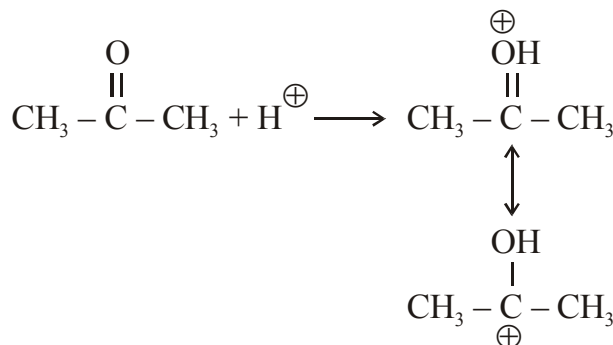


The reason is that the C = O double bond of a carbonyl group is stronger bond ($> \text{C} = \text{O}$, 364 kJ/mole) than the C = C (bond strength 250 kJ/mole) of the enol. However, some enols are more stable than their corresponding carbonyl compounds. Phenol is formally an enol, but the enol form of phenol is more stable than its two keto tautomers because phenol is aromatic.

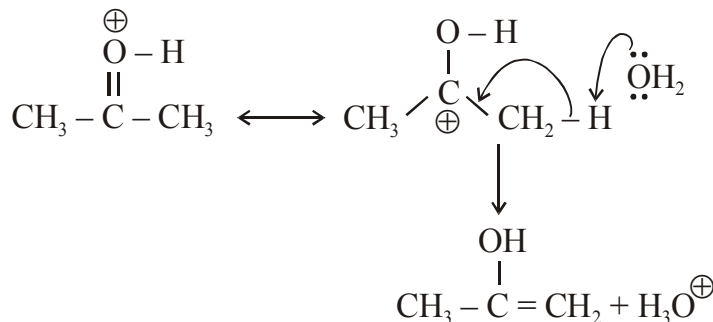


The mechanism for the interconversion of the keto and enol tautomers in acidic medium is shown below :

Step-I :

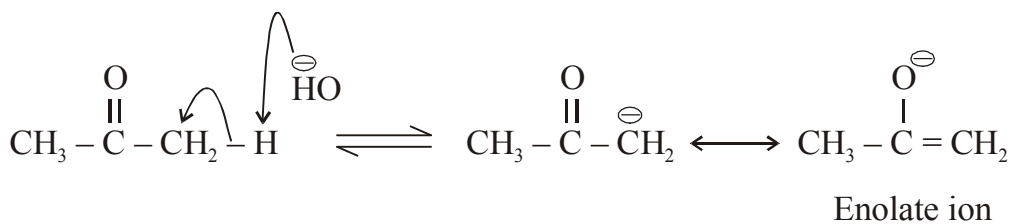


Step-II :

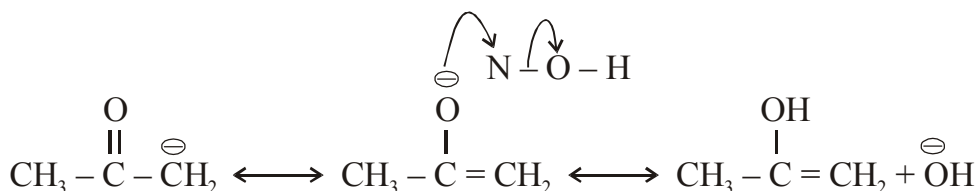


The mechanism for enolisation in basic medium is as follows :-

Step-I :



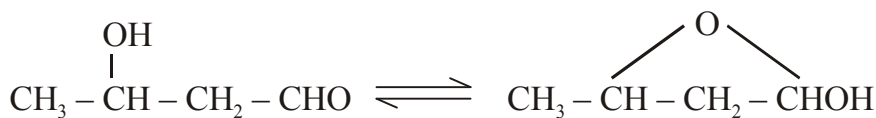
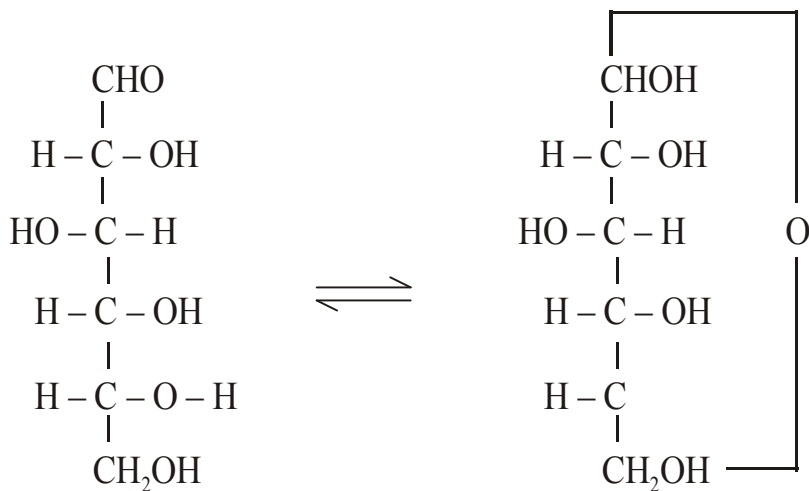
Step-II :



2. Ring-Chain Tautomerism :

In some cases migration of hydrogen results in a ring formation. Thus tautomerism in which one form is cyclic and other is open-chain is called ring-chain tautomerism.

Examples are :



1.8 Aromaticity or Aromatic Character

Benzene is the aromatic compound of for excellence. Relatively few compounds possess benzene like properties. Thus, aromatic compounds are those which resemble benzene in chemical behaviour.

Benzene has special stability in comparison to aliphatic conjugated trienes. The stability of benzene can be known by its resonance or delocalisation energy. There are three experimental procedures for the determination of the magnitude of the resonance energy. Here will be discuss only two methods for the determination of resonance energy of benzene.

(i) Heat of Hydrogenation :

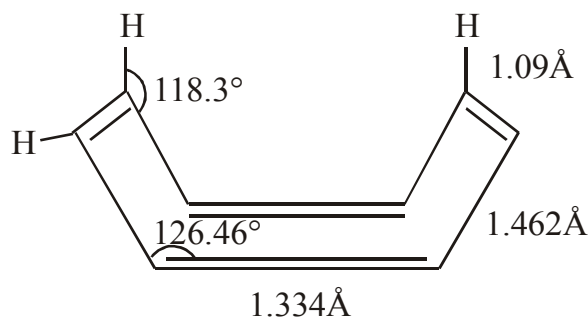
The heat of hydrogenation of cis-2-butene is -28.6 kcal/cyclohexene can also be treated as cis-2. butene derivative. Heat of hydrogenation of cyclohexene is also -28.6 kcal/mole. Thus heat of hydrogenation for one double bond in cyclic system can be taken as -28.6 kcal/mole per double and the predicted value is $-2 \times 28.6 = -57.2$ Kcal/Mol. Thus, have the same empirical formula of both the compounds are the same bond as standard value. This guess is very close to correct; the heat of hydrogenation of 1,3 of cyclohexadiene is -55.4 kcal/mole.

Thus, there is no special affect apparent from confining two double bonds in a six membered ring. Thus, conjugation in 1,3- cyclohexadiene does not increase the stability because observed heat of hydrogenation for 1,3-cyclohexadiene is -55.4 kcal /mole Thus the heat of hydrogenation for per double bond in 1,3- cyclohexadiene would be $-55.4/2 = -27.7$ kcal/mole.

Now, let us calculate heat of hydrogenation for 1,3,5-cyclohexatriene, the hypothetical molecule with three double bonds in a six membered ring. The predicted heat of hydrogenation for this hypothetical molecule in comparison to 1,3- cyclohexadiene would be $-27.7 \times 3 = -83.1$ kcal/mole. The measured heat of hdyrogenation for bennene is -49.3 kcal/mole. This measured value is much lower than the calculated value for 1,3,5- cyclohexatriene. The difference between calculated and measured heat of hydrogenation is $-83.1 - (-49.3) = -33.8$ kcal/mole. This difference represents the amount of energy the special stabilisation of benzene is worth. This differnce is called the resonance energy or delocalisation energy of benzene. This resonance energy indicates the special stability of the benzene molecule.

(ii) Heat of formation:

Let us examine the stability of benzene using heats of formation. Since benzene, C_6H_6 , and cyclooctatetraene (COT) C_8H_8 + their heats of formation per CH group can be compared. Although empirical formula of both the compounds are the same, their structures are remarkably different. First COT has alternate single and double bounds. Second COT is not planar like benzene, instead it is tub-shaped. Thus COT look like four isolated ethylene molecule.



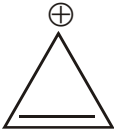
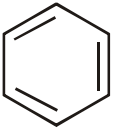
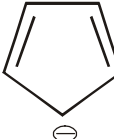
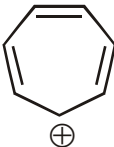
The ΔH_f° of benzene is + 19.82 kcal/mole or $19.82/6 = 3.3$ kcal / CH group. The ΔH_f° for COT is + 71.23 kcal/mole or $71.23/8 = 8.9$ kcal per CH group. This means that per CH group, benzene is $8.9 - 3.3 = 5.6$ kcal/mole more stable than COT. It follows, then that benzene is $5.6 \times 6 = 33.6$ kcal/mole more stable than a hypothetical six carbon cyclic triene with the same stability as COT. This energy difference of about 34 kcal/mole is called the empirical resonance energy of benzene.

This special stability has come to be known as benzene's aromatic character or aromaticity.

1.8.1 Aromatic Compounds.

According to Huckel rule planar monocyclic completely conjugated hydrocarbons will be aromatic when the ring contains $(4n + 2)\pi$ electrons. In $(4n+2)$, n may be any integer 0,1,2,3,.....

The value of $(4n+2)\pi$ conjugated electrons is known as Huckel number. Some examples are :

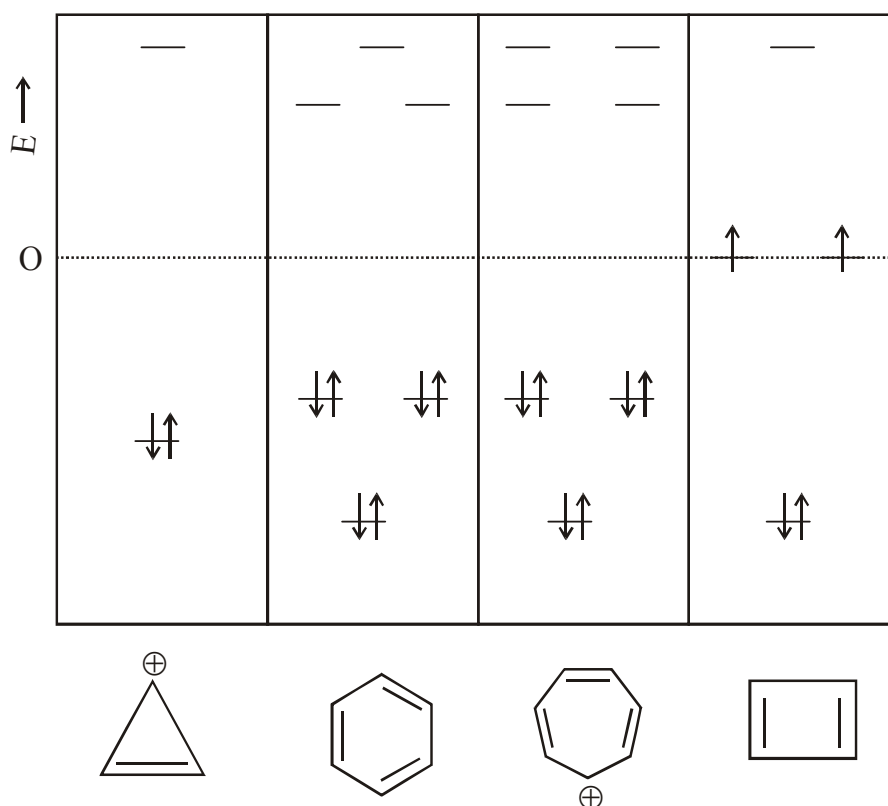
Structure	$(4n + 2)\pi$	n
	2	0
	6	1
	6	1
	6	1

According to molecular orbital energy levels, aromaticity is observed when all bonding molecular orbitals are filled and non-bonding molecular orbitals, if present, are empty, or completely filled.

1.8.2. Antiaromatic Compounds

According to the Huckel rule planer monocyclic completely conjugated hydrocarbons

will be antiaromatic when the ring contains $(4n)\pi$ electrons, where n is any interger, 1,2,3, 4



Filling of electrons in HMO π energy level diagrams of Annulenes.

In terms of molecular orbital energy levels a species is antiaromatic if it has electrons in antibonding molecular orbitals, or if it has half filled molecular orbitals or half ifled non-bonding molecular orbitals provided it is planer.

1.8.3. Nonbenzenoid Aromatic Compounds

A benzenoid aromatic compound is defined as that compound which does not have a benzenoid ring but exhibits a degree of aromatic character typical of benzene. Aromaticity of non-benzenoid compounds can be known by Huckels rule and Craig's rule. Huckels rule is used in monocyclic polyenes whereas Craig's rule is used in bicyclic and polycyclic polyenes.

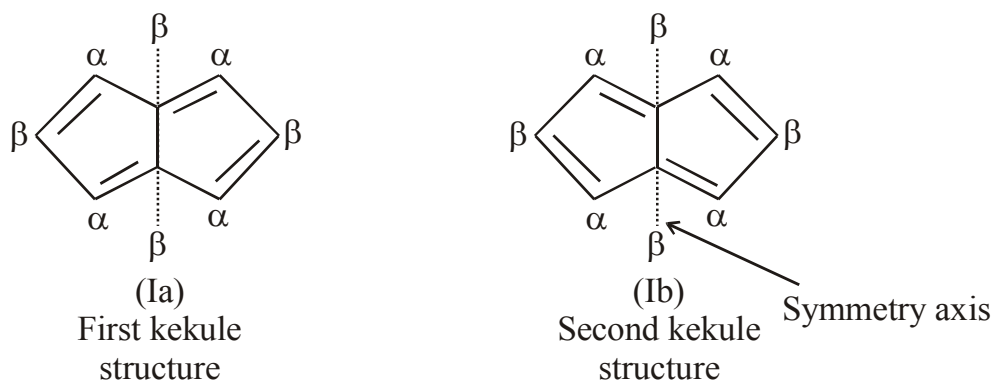
According to Huckel's rule monocyclic, coplanar system of trigonally hybridised atoms which contain $(4n+2)\pi$ electrons are aromatic in character. This means that planar system having 2,6,10,14,18 or 22 π -electrons may be expected to be aromatic. The cyclopropenium cation, the cyclopentadienide anion, the cycloheptatrienium cation, [14] annulene and [18]

annulene, for example, should therefore be aromatic provided they are planar, but cyclobutadiene, cyclooctatetraene and [12] annulene should be non-aromatic even if they are planar molecule.

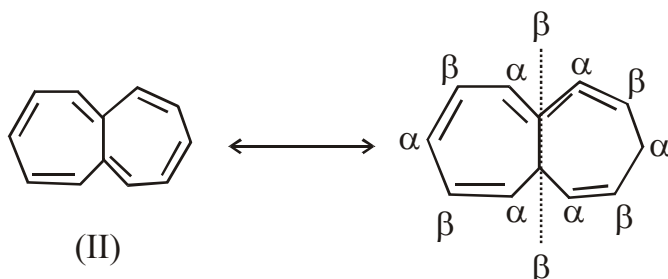
Huckel rule is of limited applicability as it is concerned only with monocyclic systems. Huckel's rule can not be applicable in bicyclic and polycyclic non benzenoid hydrocarbons which have classical structures with alternate single and double bonds.

Craig has proposed an empirical rule but the rule applies only to those hydrocarbons in which at least two centres be on a symmetry axis that converts one kekule type structure to another. The structural formula is first labelled with equal numbers of spin symbols α and β , as far as possible alternately, different symbols being given to the ends of all double bonds in the kekule type structure. The sum is then taken of the number (f) of symmetrically related π -centres not on the symmetry axis, and the number (g) of inter conversions of α and β by rotation about the axis. If this sum, $f+g$ is even, the valence bond ground state is symmetric. If the sum is odd, the compound may be expected to be non-aromatic.

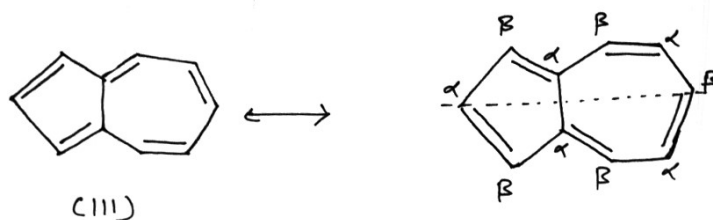
In pentalene (I), for example, three pairs of centres are related by the symmetry axis, and $f=3$. Upon rotation no interconversions of α and β occur; i.e. $g = 0$. Hence $f + g = 3$, odd number, and pentalene should be non-aromatic,



Consider the second example heptalene (II). For heptalene $f = 5$ and $g = 0$ so $f+g = 5$, and this hydrocarbon should be non-aromatic.



For azulene (iii) $f = 4$ and $g = 0$ so that $f+g = 4$. Thus, azulene would be expected to be aromatic. Experimentally, heptalene has been found to be an unstable non-aromatic hydrocarbon and azulene is aromatic.

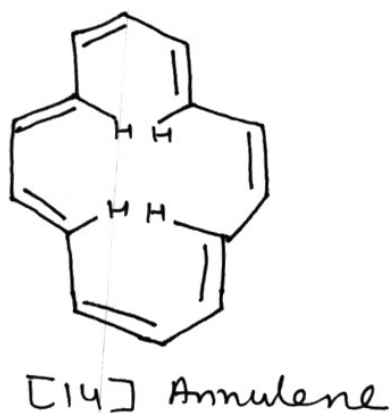
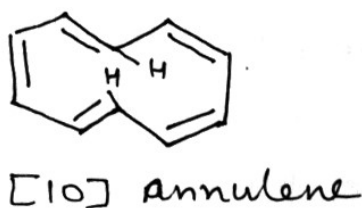


1.9 Annulenes

The monocyclic conjugated systems of the general formula $(CH)_{2m}$ have been called annulenes, the number of carbon atoms in the ring being denoted by prefixed number in brackets. In this system of nomenclature, benzene is [6] annulene and COT is [8] annulene. Since the carbon atoms occur as doubly bonded pair, an annulene must have an even number of electrons. The annulenes can be grouped into two series.

- (i) Those in which m is odd having $(4n+2)\pi$ -electrons, and
- (ii) Those in which m is even having $(4n)\pi$ electrons.

Examples :-



1.10 Alternant and Non-Alternant Hydrocarbons

Alternant Hydrocarbons :

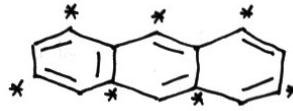
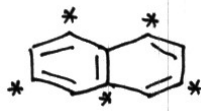
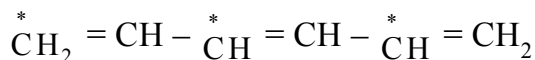
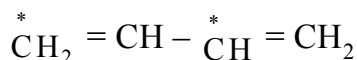
Linear conjugated chains and cyclic conjugated molecules containing only rings with even number of carbons belong to a type of molecule called alternant. An alternant system is one in which the atoms can be divided into two classes such that atoms of one class are bonded only to atoms of the other class. To determine if a hydrocarbons skeleton is alternant, put a star at an arbitrary position then alternate unstarred, starred, until all atoms have been marked. Thus in alternant hydrocarbons starred atom is always linked with unstarred atom.

Alternant hydrocarbons are of two types :

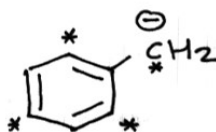
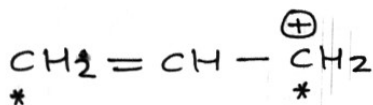
- (i) Even alternant hydrocarbons and
- (ii) Odd alternant hydrocarbons.

Even alternant hydrocarbons : Contain even number of conjugated atoms, i.e., an equal number of starred and unstarred conjugated atoms.

Examples are 1,3-butadiene, 1,3,5-hexatriene, benzene, naphthalene, anthracene, etc.



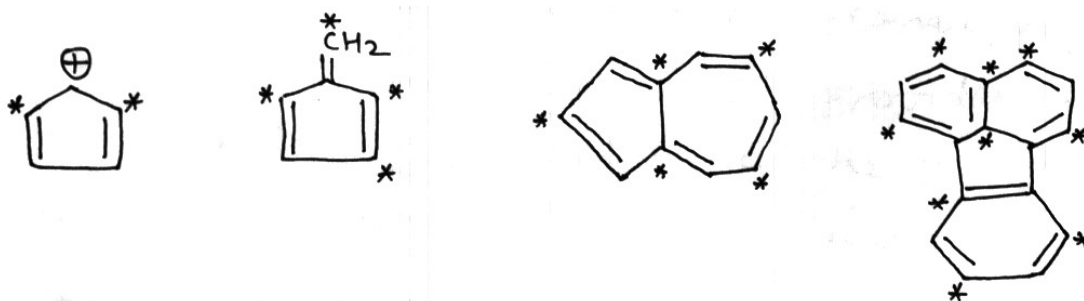
Odd alternant hydrocarbons contain odd number of conjugated atoms. Odd alternant hydrocarbons are generally carbocation, carbanion or free radical. In odd alternant hydrocarbons number of starred and unstarred conjugated atoms are not the same.



Non-alternant Hydrocarbons :

In non-alternant hydrocarbons, the conjugated atoms, whose number may be even and odd, may be divided into two sets such that two atoms of same set (say starred set) is linked to each other. If non-alternant hydrocarbon is cyclic then at least one cyclic system has odd numbers of carbons in the ring.

Examples of non-alternant hydrocarbons are :



Non-alternant hydrocarbons may be aromatic, antiaromatic or non-aromatic.

1.11 Huckel Molecular Orbital Theory : (HMO Theory)

Huckel molecular theory is applied to conjugated systems. This theory is based on the assumption that the pi-system can be treated independently of the sigma framework in conjugated planar molecule and it is the Pi system that is of paramount importance in determining the chemical and spectroscopic properties of conjugated polyenes and aromatic compounds. The basis for treating the sigma system and pi-systems as independent of each other in their orthogonality. The sigma skeleton of a planar conjugated system lies in the nodal plane of the π -system and does not interact with it. Because of the simplicity of the HMO theory this theory has been extremely valuable in the application of molecular orbital concepts to conjugated planar polyenes (open chain and cyclic). It provides a good qualitative description of the pi-molecular orbitals in both cyclic and a cyclic conjugated systems. Systems having $4n+2$ carbon atoms in the ring.

- (1) Total number of p molecular orbitals are $(4n+2)$
- (2) There is one molecular orbital lowest in energy and one molecular orbital highest in energy.
- (3) The remaining molecular orbitals will be $4n+2-2 = 4n$
- (i) Out of $4n$ molecular orbitals $2n$ will be bonding molecular orbitals and $2n$ will be antibonding molecular orbitals. These orbitals will be present in the form of pair of degenerate molecular orbitals. Let us take the example of benzene.



$(4n + 2)$ system

Total number of molecular orbitals are

$$4n+2, \text{ i.e. } 4 \times 1 + 2 = 6$$

- (ii) One bonding molecular orbital lowest in energy and one antibonding molecular orbital highest in energy.

- (iii) The remaining orbitals will be $4n+2-2$, i.e., $6-2 = 4$. Out of four molecular orbitals 2 will be bonding molecular orbitals and two will be antibonding molecular orbitals. These four molecular orbitals will be present in the form of pair of degenerate orbitals.

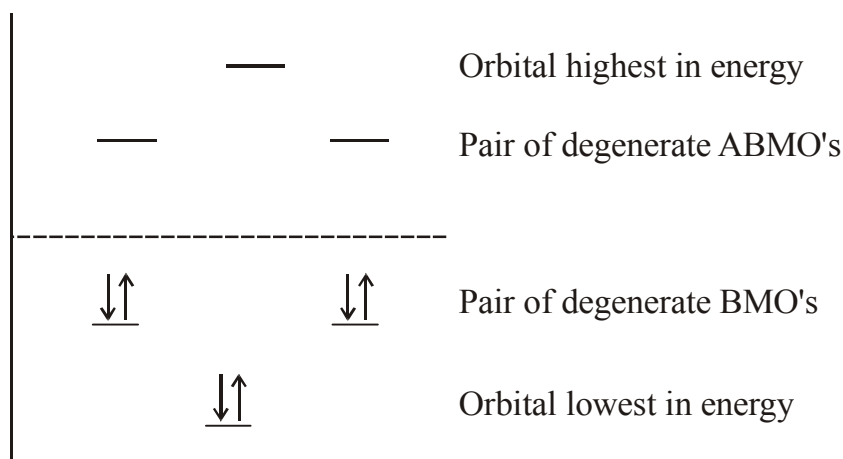


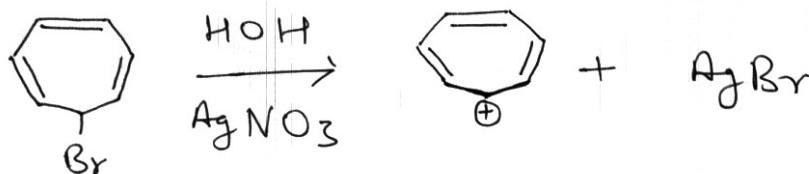
Fig. : π -molecular orbital diagram of benzene

1.12 Solved Examples

- Q.1-** 7-Bromocycloheptatriene completely dissociates in water and gives a precipitate of AgBr with AgNO₃, unlike its open chain analogue, 3-bromo-1,4-pentadiene. Explain.

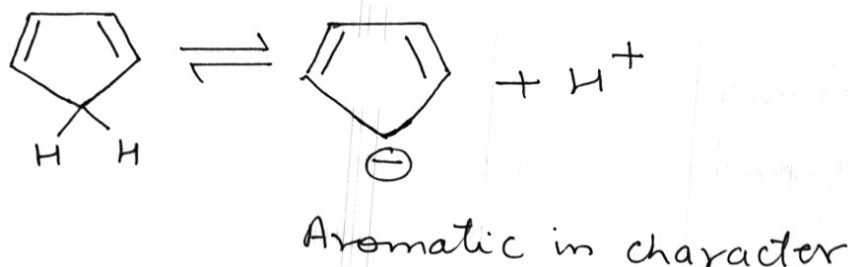
Solution -

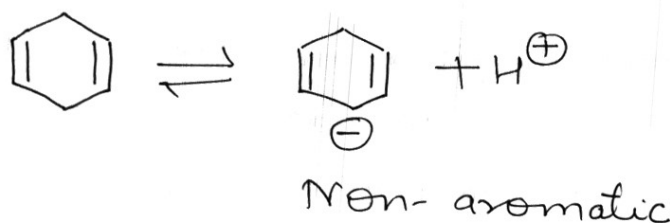
7-Bromoheptatriene on ionisation in water gives cycloheptatrienyl cation. This cation is aromatic and highly stable.



- Q.2.** Explain why cyclopentadiene is much more acidic than 1,3-cyclohexadiene.

Solution -

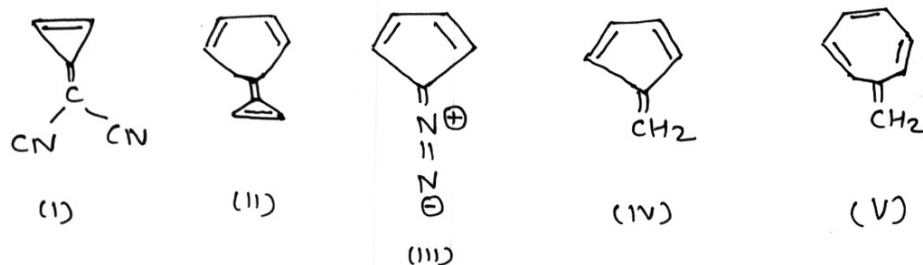




Cyclopentadiene gives aromatic anion which is highly stable where as cyclohexadiene gives anion which is non aromatic. Hence cyclopentadiene is more acidic than cyclohexadiene.

1.13 Model Questions

- Resonance energy of benzene is much more higher than 1,3-butadiene. Why?
- Heat of hydrogenation of cyclohexene to cyclohexane is -28.6 kcal/mole. The observed heat of hydrogenation of benzene to cyclohexane is -49.8 kcal/mole. Find out the resonance energy of benzene.
- Give brief account on the following.
 - Alternant and non-alternant hydrocarbons
 - Hyperconjugation.
 - Resonance.
- Discuss aromaticity of non-benzenoid aromatic compounds.
- The given compounds are aromatic or non-aromatic and why? Explain.



1.14 Reference

- Advanced organic chemistry : Dr. Jagdamba Singh and Dr. L.D.S. Yadav
- Organic Chemistry : Finar