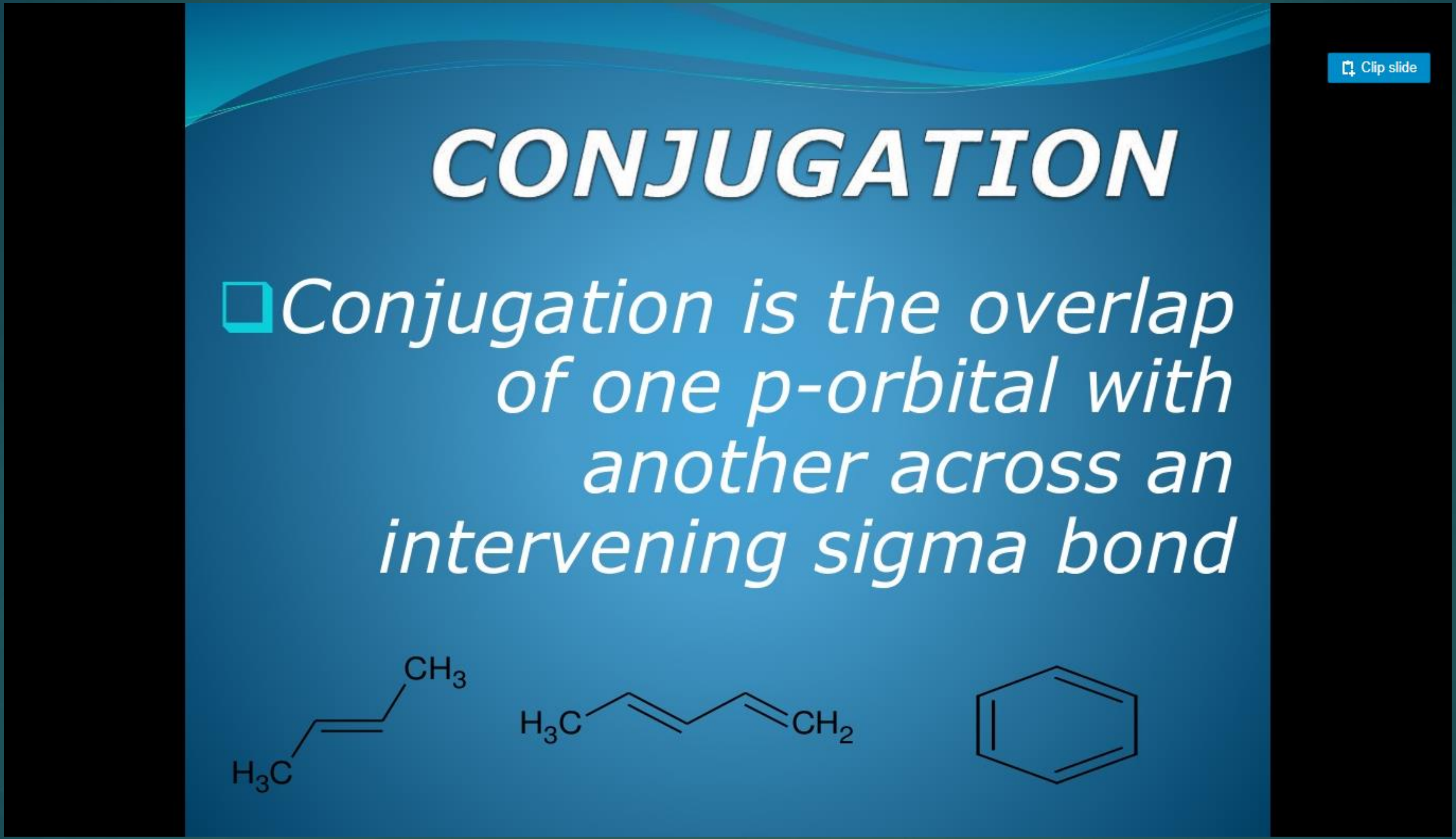
Nature of Bonding in Organic Molecules

M.Sc. SEM – 1 CHNN : 402 UNIT : 1

PRESENTED BY : DR. ZAKIR M GADHAWALA

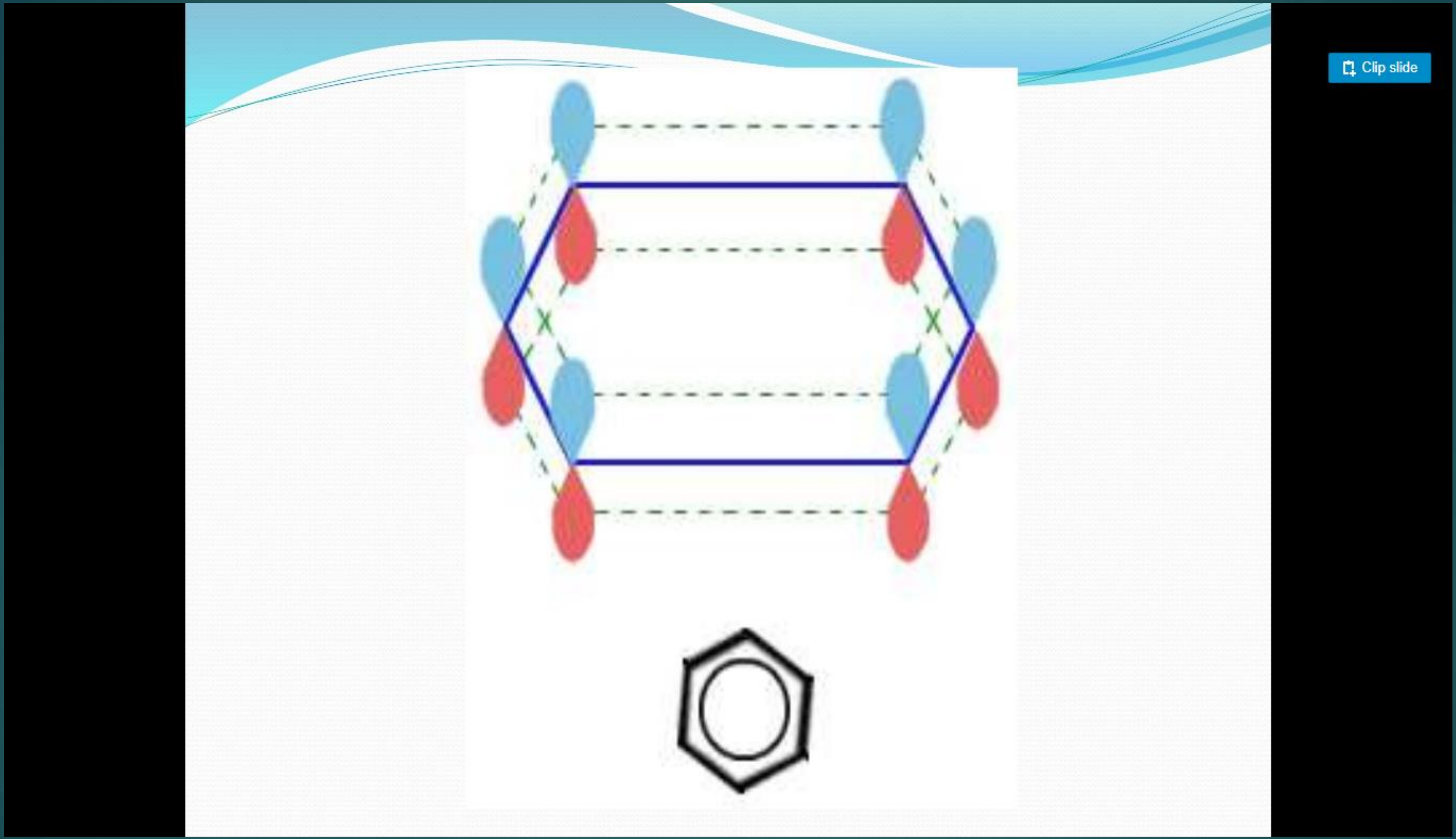
Learning Outcomes

- Conjugation, Cross Conjugation and Hyper Conjugation
- Bonding in Fullerene
- Tautomerism and types of Tautomerism
- Aromaticity in Benzenoid and Non Benzenoid Compounds
- Alternate and Non alternate hydrocarbons
- Huckel’s Rule and Aromaticity, Antiaromaticity, Homoaromaticity
- Aromaticity in Annulenes
- Crown ethers and Cryptand Complexes
- Catenanes and Rotaxanes
- Inclusion compounds and Cyclodextrins



CONJUGATION

- Conjugation is the overlap of one p-orbital with another across an intervening sigma bond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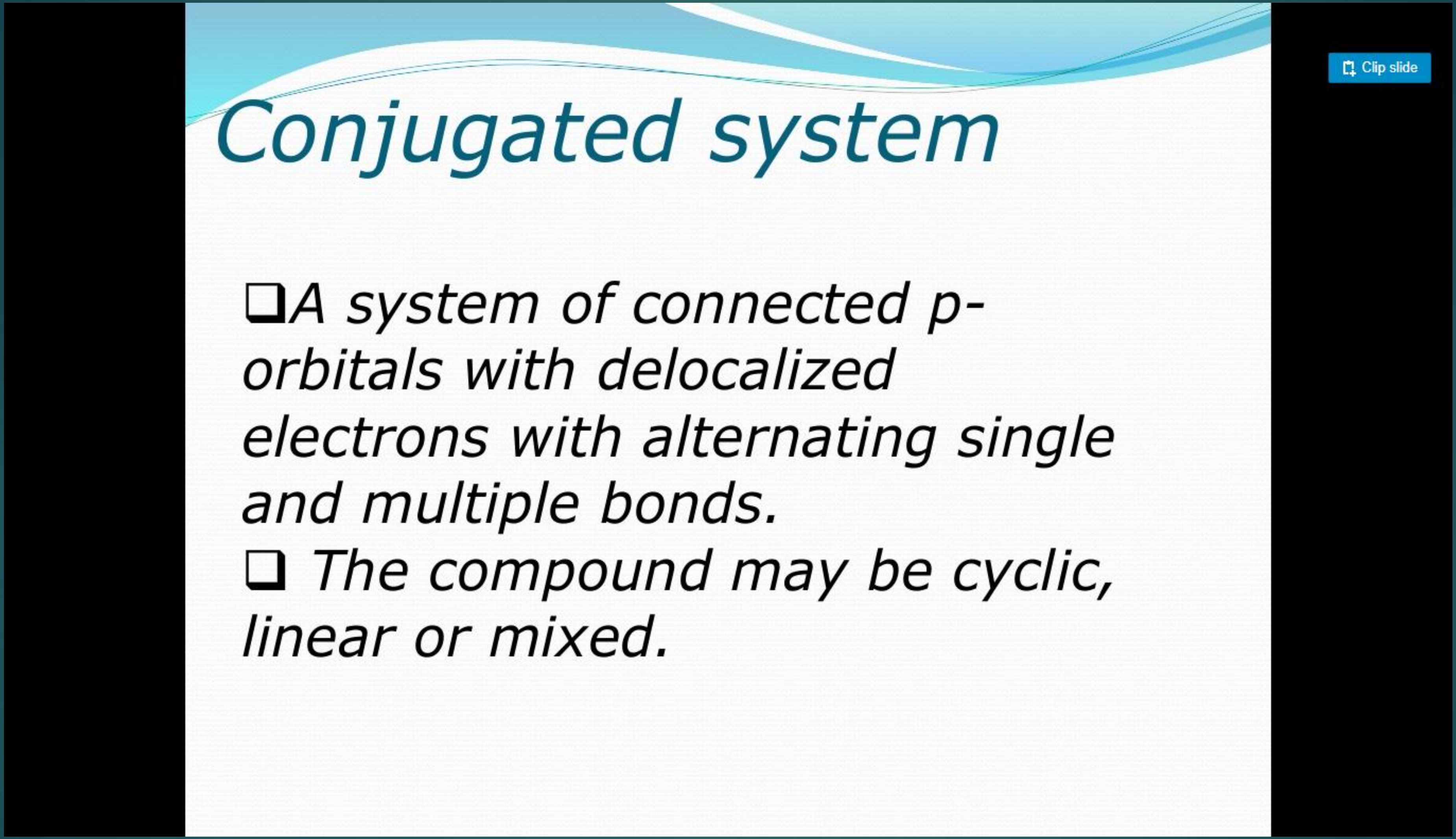
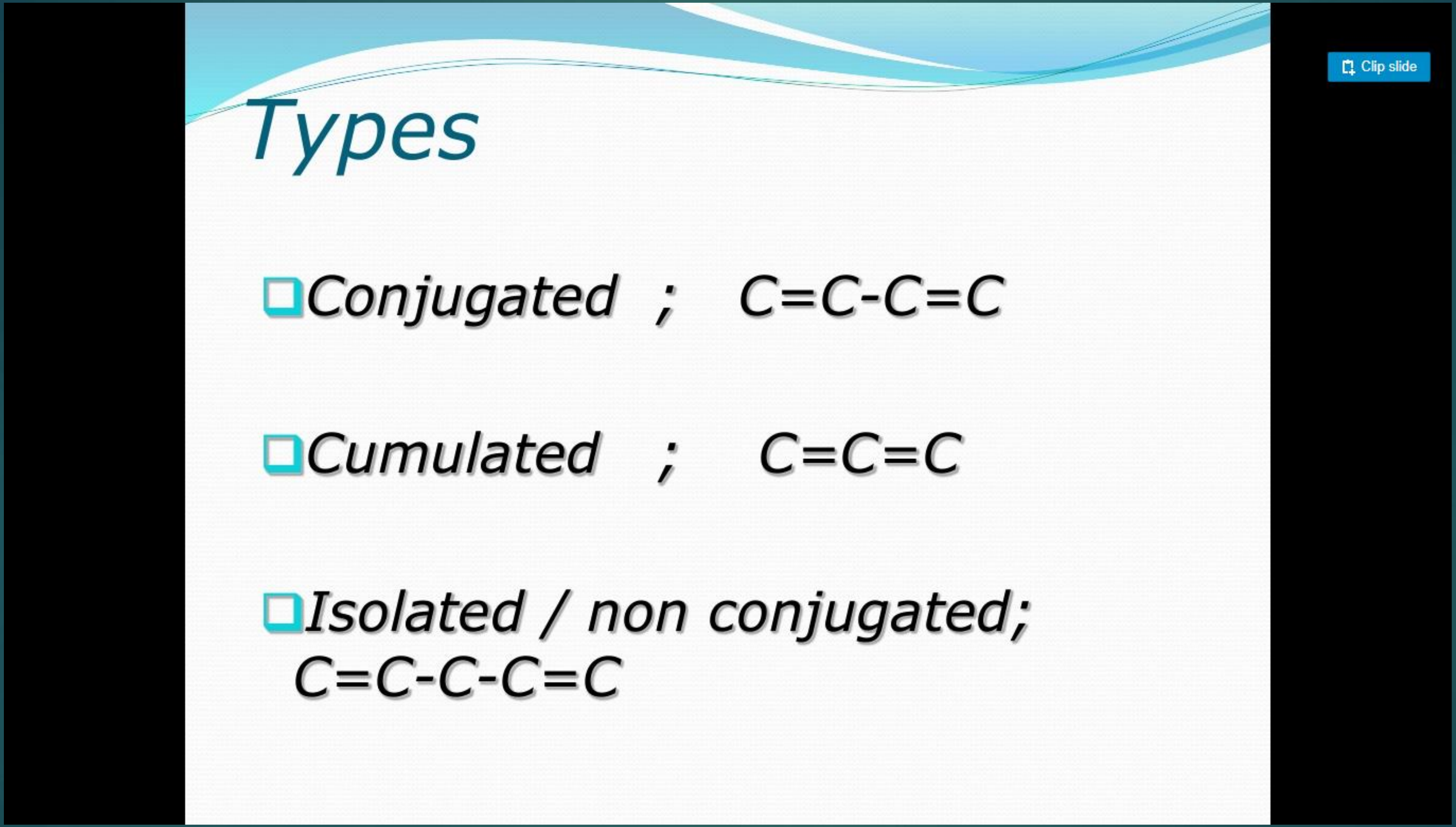


Conjugated system

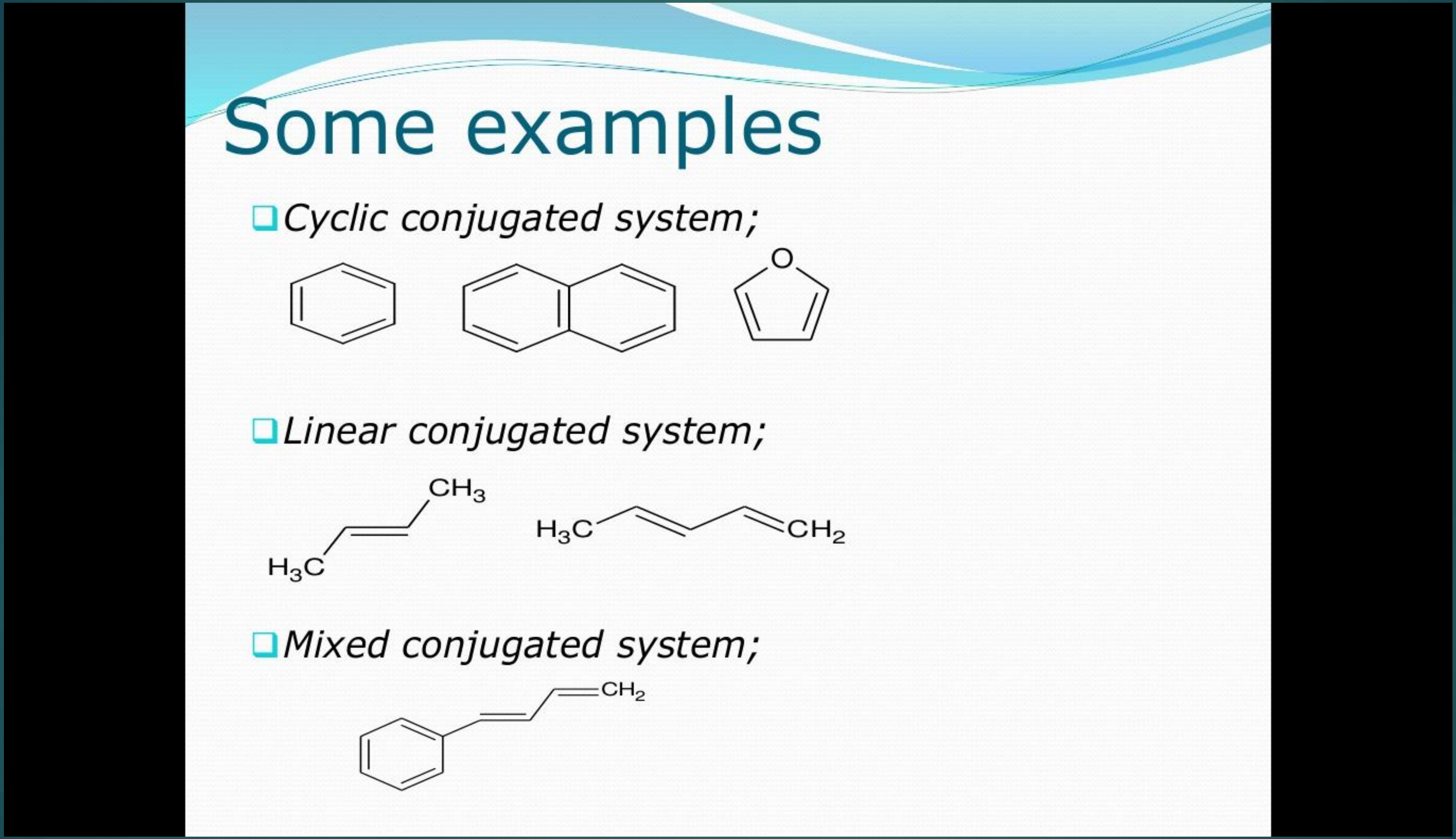
❑A system of connected p-orbitals with delocalized electrons with alternating single and multiple bonds.

❑ The compound may be cyclic, linear or mixed.



Types

- ❑Conjugated ; $C=C-C=C$
- ❑Cumulated ; $C=C=C$
- ❑Isolated / non conjugated; $C=C-C-C=C$



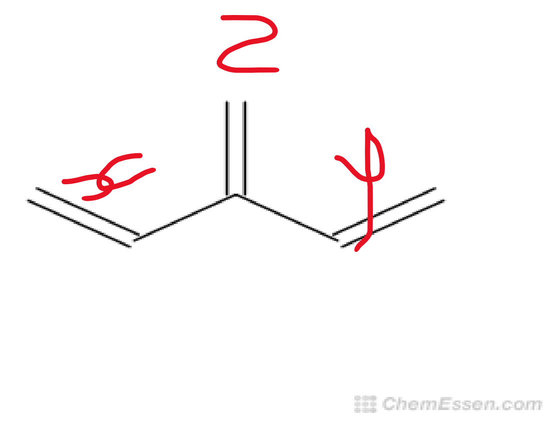
Some examples

- *Cyclic conjugated system;*
- *Linear conjugated system;*
- *Mixed conjugated system;*

Cross Conjugation :

Definition : It is a special type of conjugation in which set of three pi bonds which are present in a molecule, only two Pi bonds interact with each other by conjugation but third one is excluded from interaction. Such type of conjugation is called Cross Conjugation.

3-Methylene Penta 1,4 Diene (Dendraline) :



Here X & Z as well as Y & Z are conjugated but X & Y is not in conjugation condition. Means X & Z involve in conjugation then Y is not involve. Similarly if Z & Y involve in conjugation then X is not involve. Such type of phenomenon is called cross conjugation.

CROSS CONJUGATION.....

In cross-conjugation three groups are present in compounds. From this two of which are not conjugated with each other. Moreover each is conjugated with the third group. e.g.

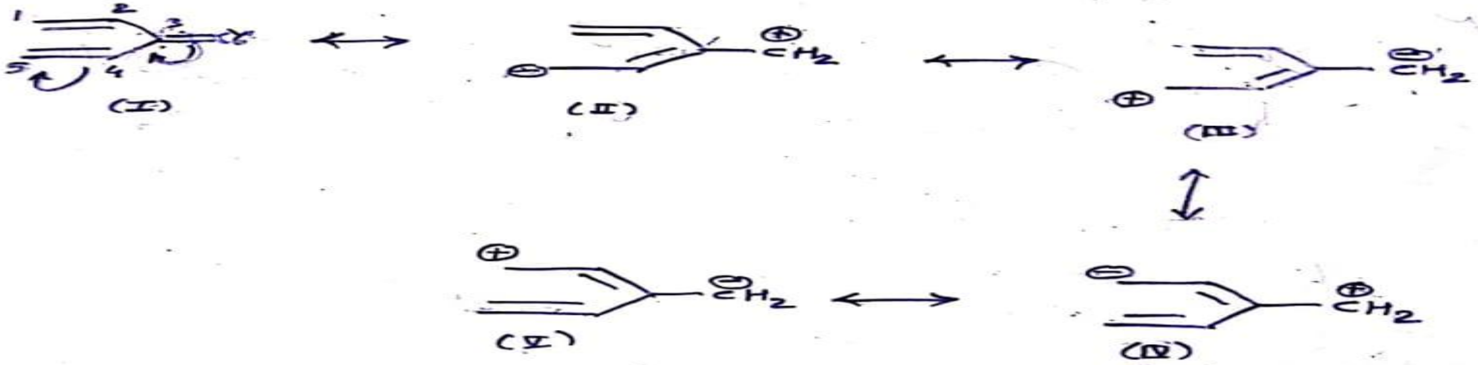
(1) (2)

& $CH_2=CH-\ddot{N}H-CH=CH_2$ (3)

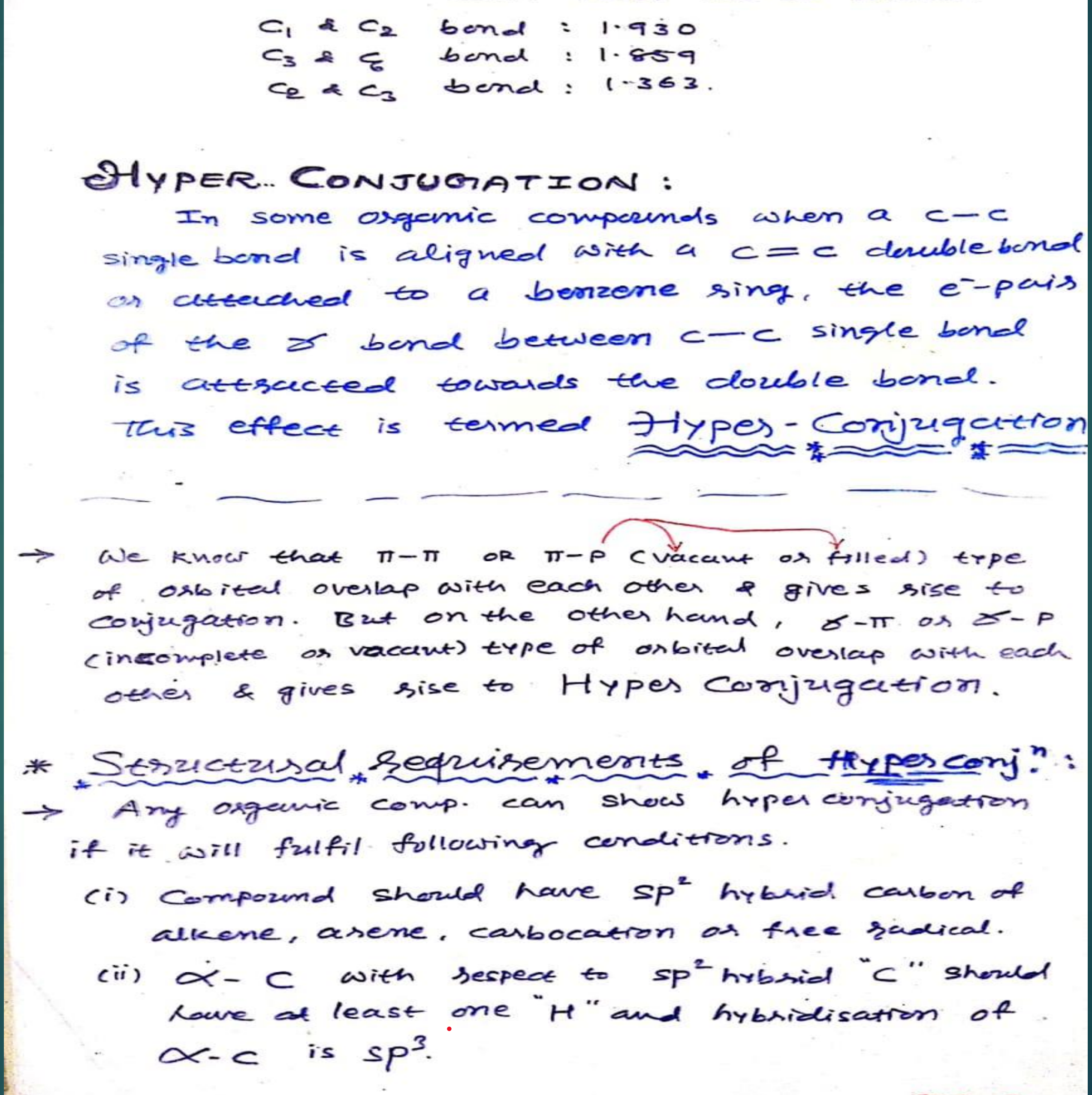
In example (1) 1 & 2 are not conjugated but third one is conjugated with 1 & 2. Cross conjugated trienes are known as dendralenes.

→ In example (2) >C=O group is conjugated with both the rings, but both rings are not in conjugation to each other.

→ In exa. (3) lone pair e^- are present on "N" is in conjugated position to both double bonds but both double bonds are not in ~~ ~~ conjugation to each other.



Here, C_1 & C_2 (OR C_4 & C_5) bonds is double bond in three (I, II, III) out of the five resonating structures while C_3 & C_6 bond is double only in one resonating



structure (I). The bond order are as follows.

C_1 & C_2 bond : 1·930
C_3 & C_6 bond : 1·859
C_2 & C_3 bond : 1·363.

HYPER CONJUGATION :

In some organic compounds when a C—C single bond is aligned with a C=C double bond or attached to a benzene ring, the e^--pair of the σ bond between C—C single bond is attracted towards the double bond. This effect is termed Hyper-Conjugation

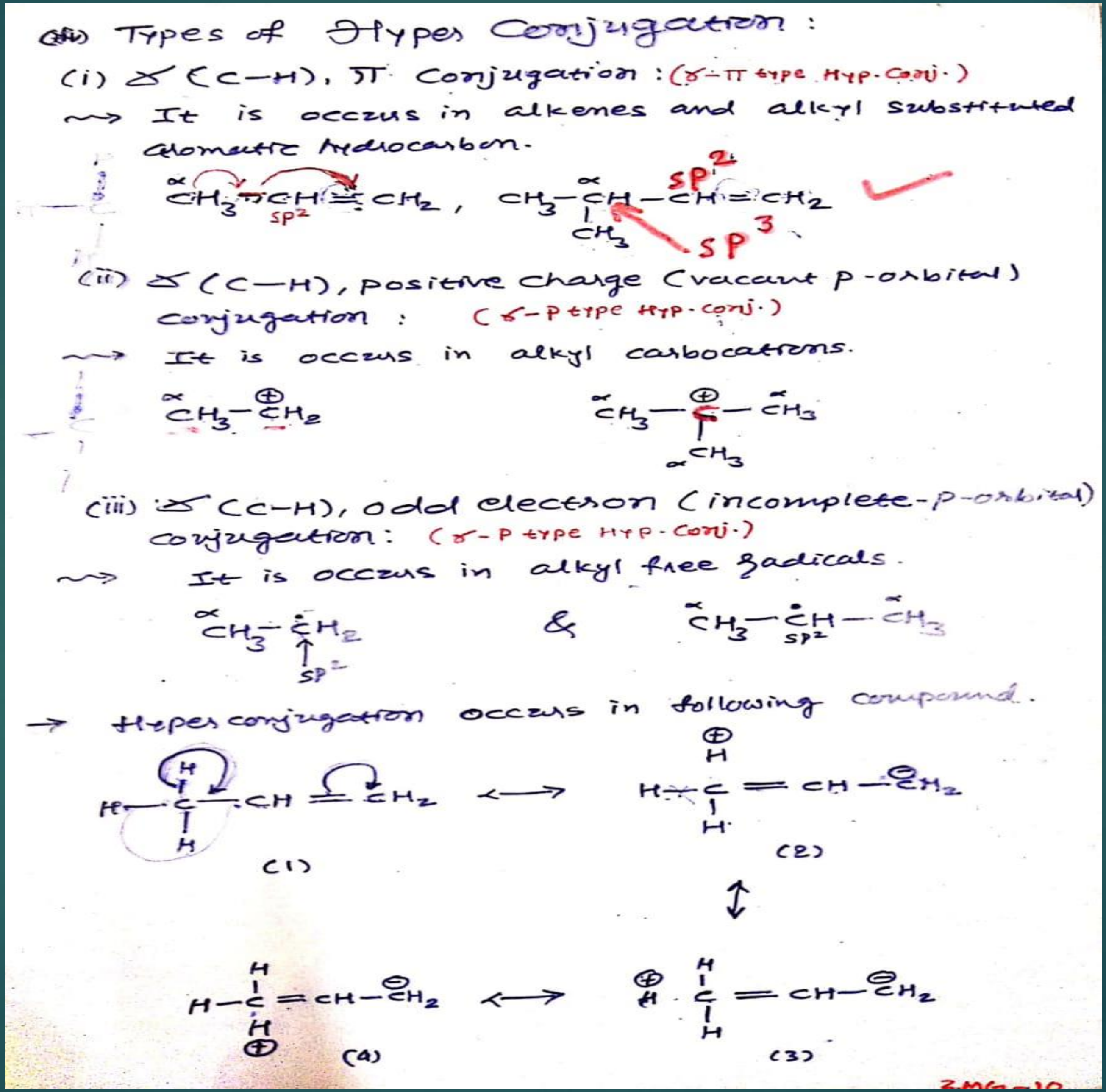
→ We know that π—π or π—p (vacant or filled) type of orbital overlap with each other & gives rise to conjugation. But on the other hand, σ-π or σ-p (incomplete or vacant) type of orbital overlap with each other & gives rise to Hyper Conjugation.

* Structural Requirements of Hyperconj^n :

→ Any organic comp. can show hyper conjugation if it will fulfil following conditions.

(i) Compound should have sp^2 hybrid carbon of alkene, arene, carbocation or free radical.

(ii) α-C with respect to sp^2 hybrid "C" should have at least one "H" and hybridisation of α-C is sp^3.



(iv) Types of Hyper Conjugation :

(i) σ (C—H), π Conjugation : (σ–π type Hyp. Conj.)

⟶ It is occurs in alkenes and alkyl substituted aromatic hydrocarbon.

$\overset{\alpha}{C}H_3-\underset{sp^2}{C}H=CH_2$, $CH_3-\underset{\underset{CH_3}{|}}{\overset{\alpha}{C}H}-CH=CH_2$ sp² sp³

(ii) σ (C—H), positive charge (vacant p-orbital) conjugation : (σ–p type Hyp. conj.)

⟶ It is occurs in alkyl carbocations.

$\overset{\alpha}{C}H_3-\overset{\oplus}{C}H_2$ $\overset{\alpha}{C}H_3-\underset{\underset{\alpha CH_3}{|}}{\overset{\oplus}{C}}-\overset{\alpha}{C}H_3$

(iii) σ (C–H), odd electron (incomplete-p-orbital) conjugation: (σ–p type Hyp. Conj.)

⟶ It is occurs in alkyl free radicals.

$\overset{\alpha}{C}H_3-\underset{\uparrow sp^2}{\dot{C}}H_2$ & $\overset{\alpha}{C}H_3-\underset{sp^2}{\dot{C}}H-\overset{\alpha}{C}H_3$

→ Hyperconjugation occurs in following compound.

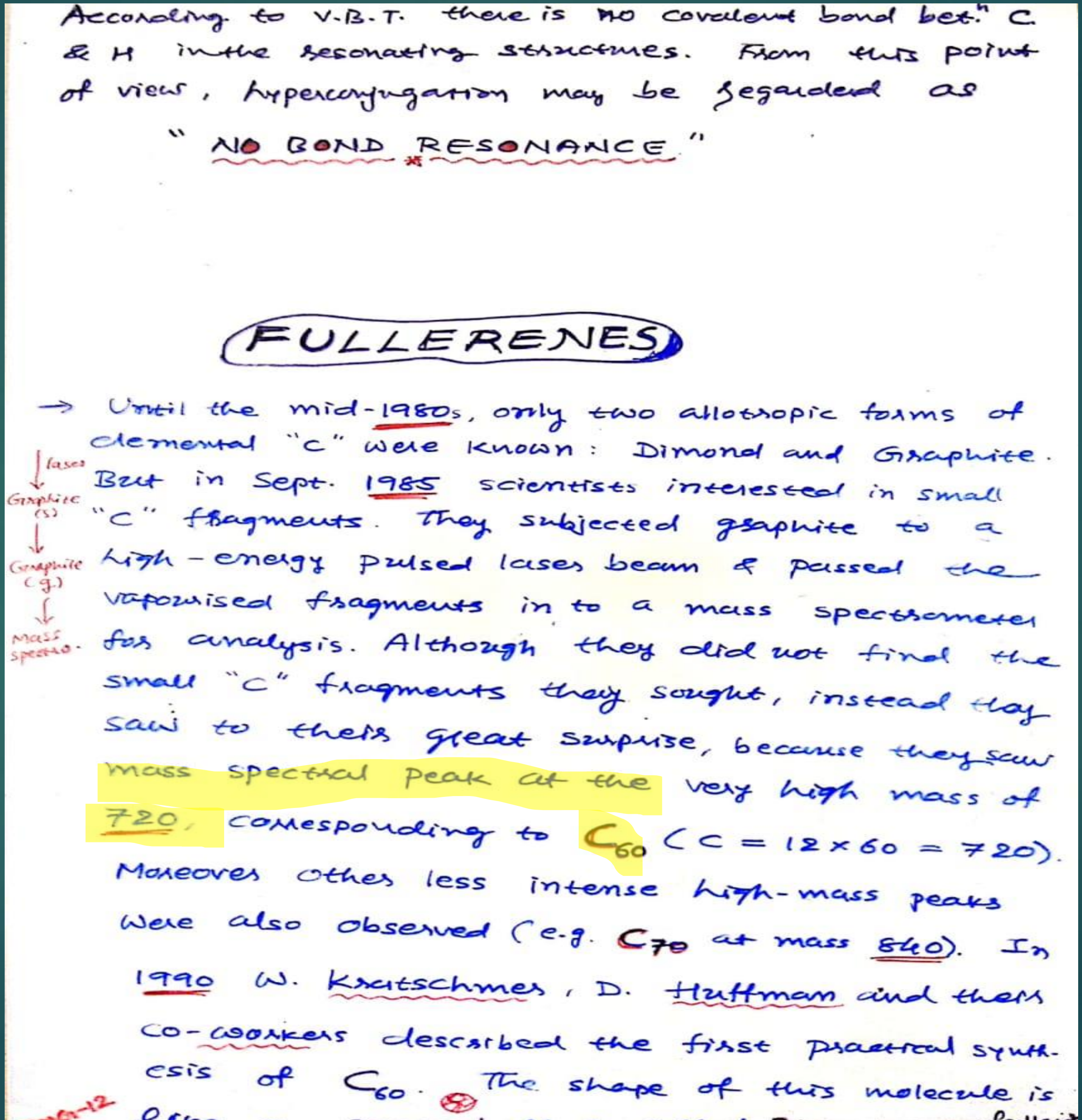
$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-CH=CH_2 \longleftrightarrow H-\underset{\underset{H}{|}}{\overset{\overset{\oplus}{H}}{C}}=CH-\overset{\ominus}{C}H_2$$

(1) (2)

$\updownarrow$

$$H-\underset{\underset{\overset{H}{\oplus}}{}}{\overset{\overset{H}{|}}{C}}=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\oplus}{H}\;\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}=CH-\overset{\ominus}{C}H_2$$

(4) (3)



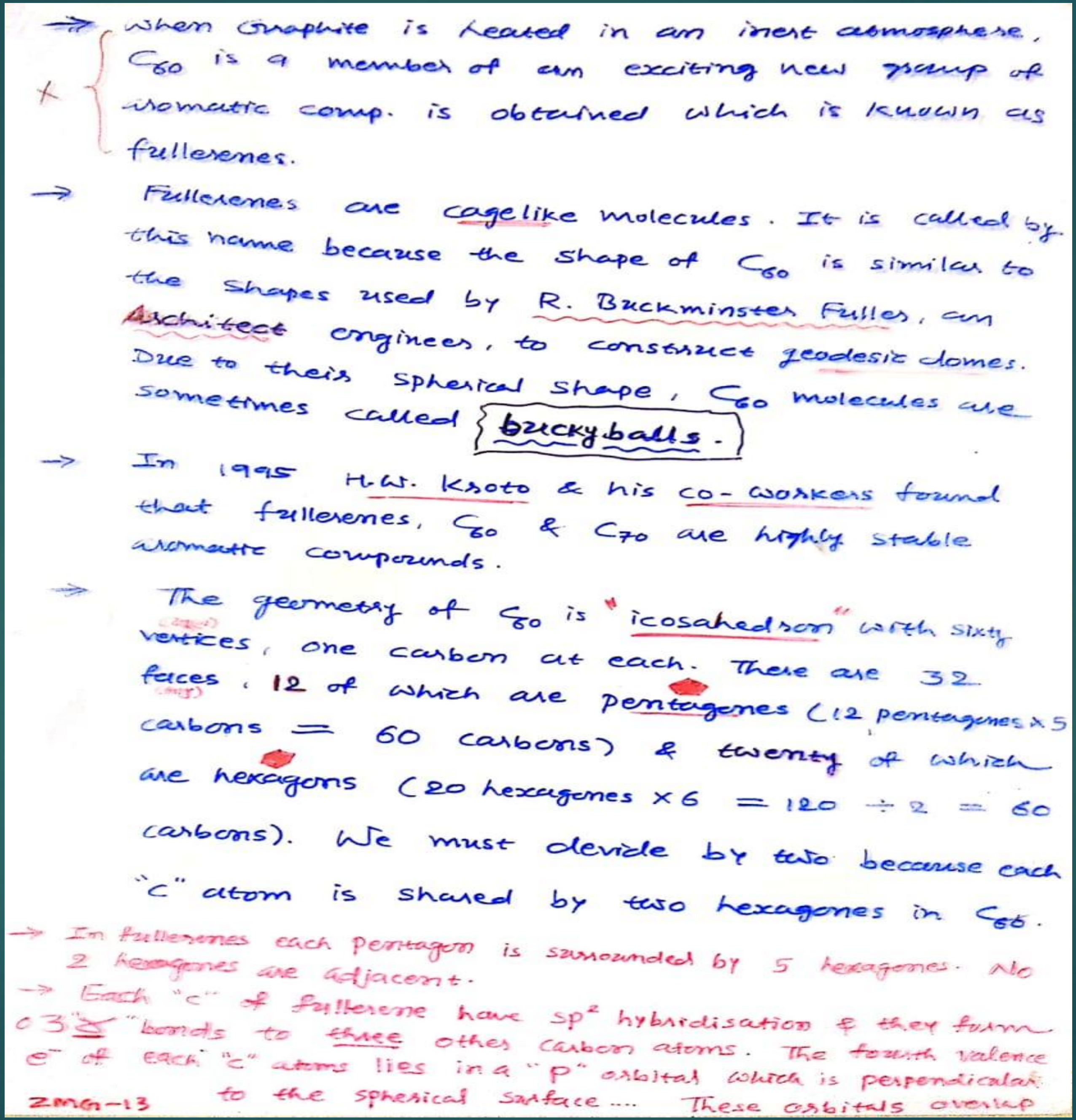
According to V.B.T. there is NO covalent bond betⁿ C & H in the resonating structures. From this point of view, hyperconjugation may be regarded as

"NO BOND RESONANCE"

FULLERENES

laser
↓
Graphite (s)
↓
Graphite (g)
↓
Mass spectro.

→ Until the mid-1980s, only two allotropic forms of elemental "C" were known: Dimond and Graphite. But in Sept. 1985 scientists interested in small "C" fragments. They subjected graphite to a high-energy pulsed laser beam & passed the vaporised fragments in to a mass spectrometer for analysis. Although they did not find the small "C" fragments they sought, instead they saw to their great surprise, because they saw mass spectral peak at the very high mass of 720, corresponding to C_{60} ($C = 12 \times 60 = 720$). Moreover other less intense high-mass peaks were also observed (e.g. C_{70} at mass 840). In 1990 W. Kratschmer, D. Huffman and their co-workers described the first practical synthesis of C_{60}. The shape of this molecule is



→ When Graphite is heated in an inert atmosphere, C_{60} is a member of an exciting new group of aromatic comp. is obtained which is known as fullerenes.

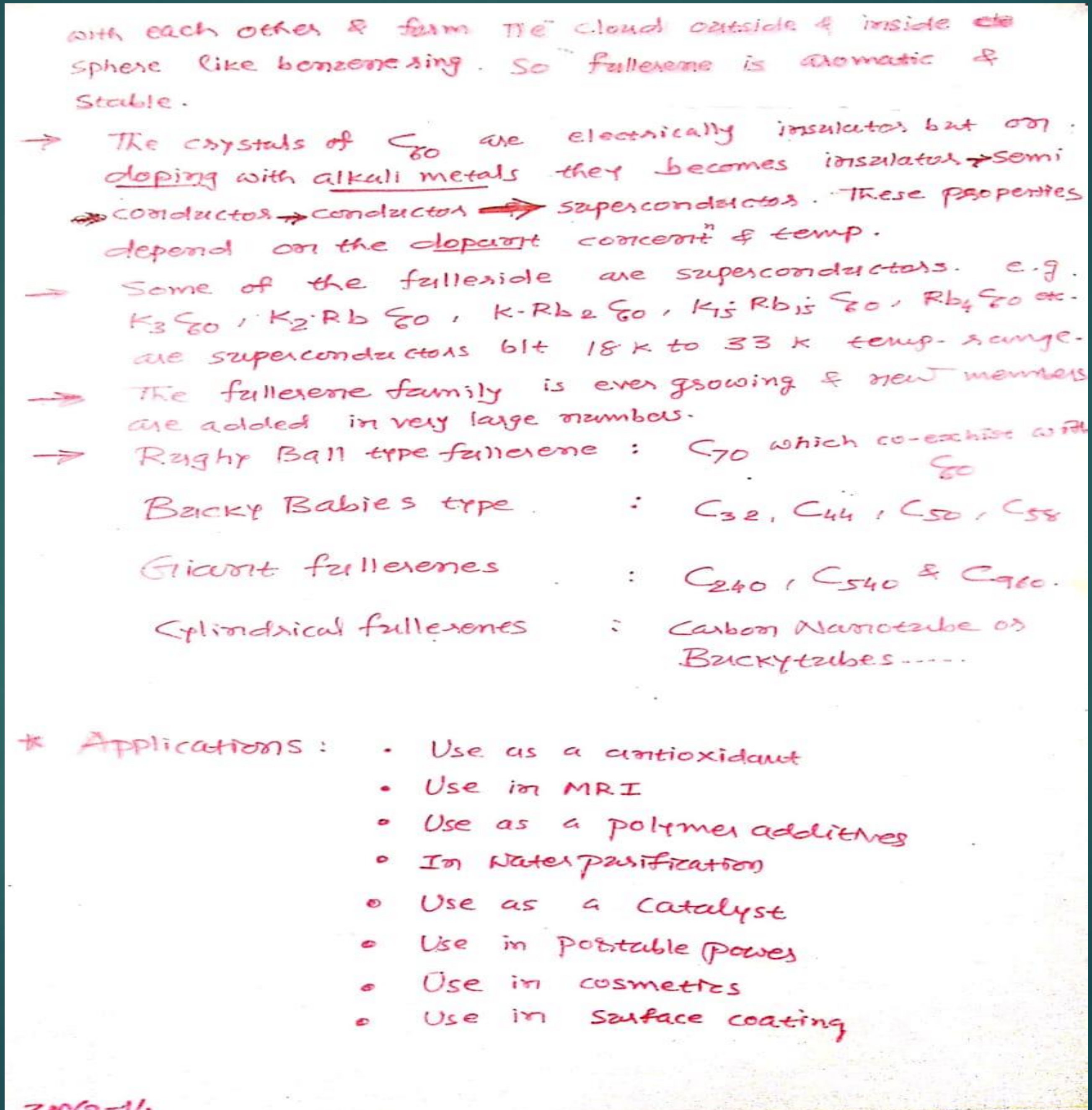
→ Fullerenes are cagelike molecules. It is called by this name because the shape of C_{60} is similar to the shapes used by R. Buckminster Fuller, an Architect engineer, to construct geodesic domes. Due to their spherical shape, C_{60} molecules are sometimes called **buckyballs**.

→ In 1995 H.W. Kroto & his co-workers found that fullerenes, C_{60} & C_{70} are highly stable aromatic compounds.

→ The geometry of C_{60} is "icosahedron" with sixty vertices, one carbon at each. There are 32 faces, 12 of which are pentagones (12 pentagones × 5 carbons = 60 carbons) & twenty of which are hexagons (20 hexagones × 6 = 120 ÷ 2 = 60 carbons). We must devide by two because each "C" atom is shared by two hexagones in C_{60}.

→ In fullerenes each pentagon is surrounded by 5 hexagones. No 2 hexagones are adjacent.

→ Each "C" of fullerene have sp^2 hybridisation & they form 3 "σ" bonds to three other carbon atoms. The fourth valence e^- of each "C" atoms lies in a "p" orbital which is perpendicular to the spherical surface.... These orbitals overlap



with each other & form the cloud outside & inside the sphere like benzene ring. So fullerene is aromatic & stable.

→ The crystals of C_{60} are electrically insulator but on doping with alkali metals they becomes insulator → semi conductor → conductor ⟹ superconductor. These properties depend on the dopant concentⁿ & temp.

→ Some of the fulleride are superconductors. e.g. K_3C_{60}, K_2RbC_{60}, KRb_2C_{60}, $K_{1.5}Rb_{1.5}C_{60}$, Rb_4C_{60} etc. are superconductors b/t 18 K to 33 K temp. range.

→ The fullerene family is ever growing & new members are added in very large numbers.

→ Rugby Ball type fullerene : C_{70} which co-exist with C_{60}

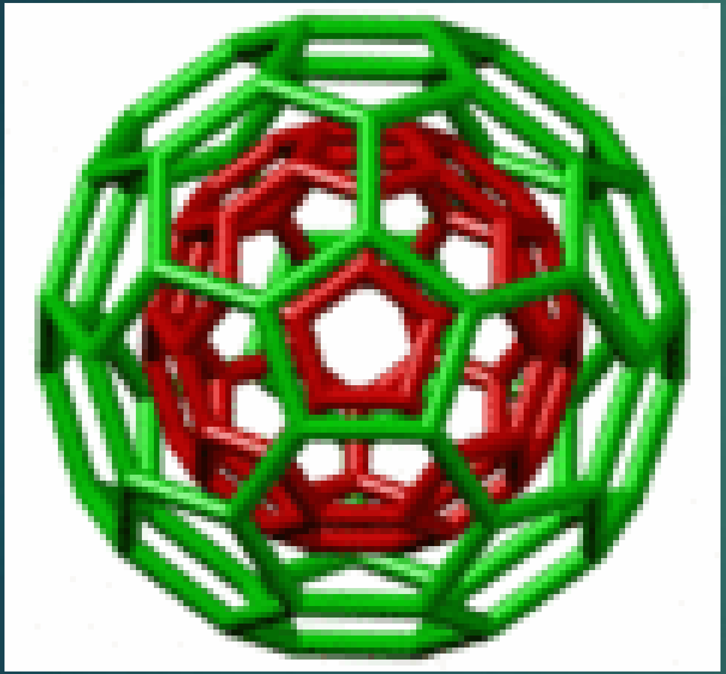
Bucky Babies type : C_{32}, C_{44}, C_{50}, C_{58}

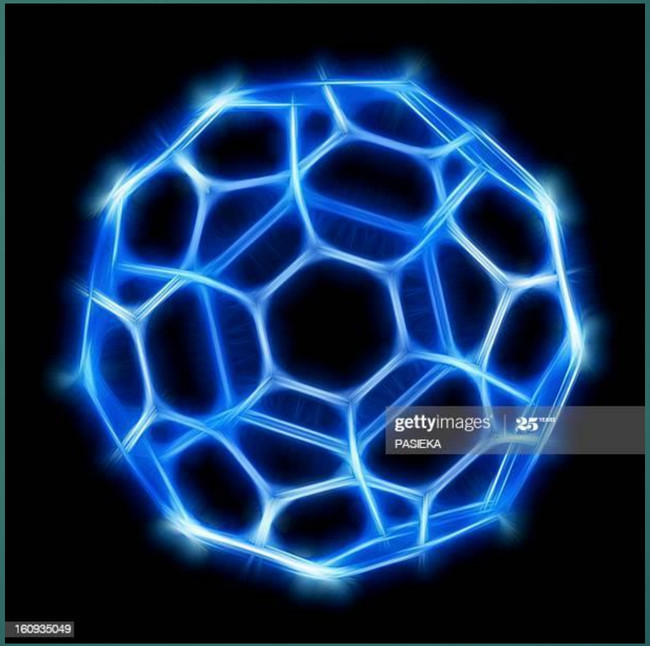
Giant fullerenes : C_{240}, C_{540} & C_{960}.

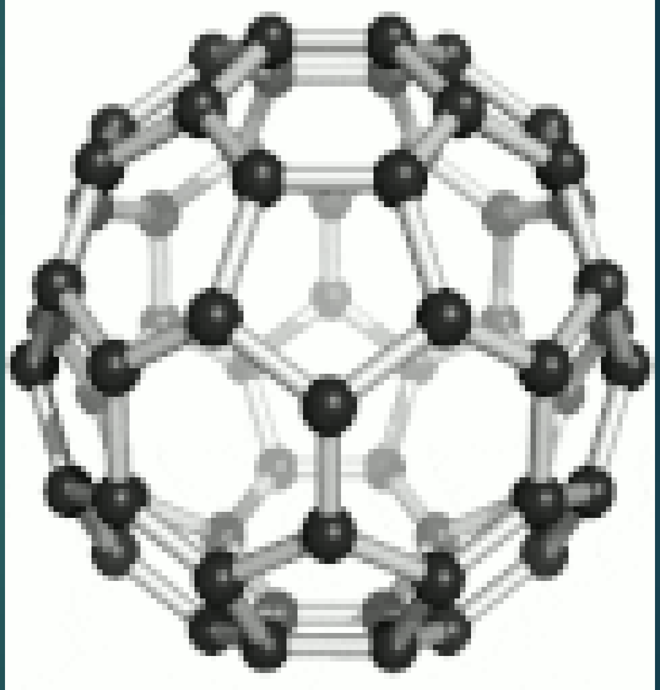
Cylindrical fullerenes : Carbon Nanotube or Buckytubes.....

* Applications :
- Use as a antioxidant
- Use in MRI
- Use as a polymer additives
- In Water purification
- Use as a Catalyst
- Use in portable power
- Use in cosmetics
- Use in surface coating

FULLERENE STRUCTURES







- https://www.youtube.com/results?search_query=%23comparisonofconjugation

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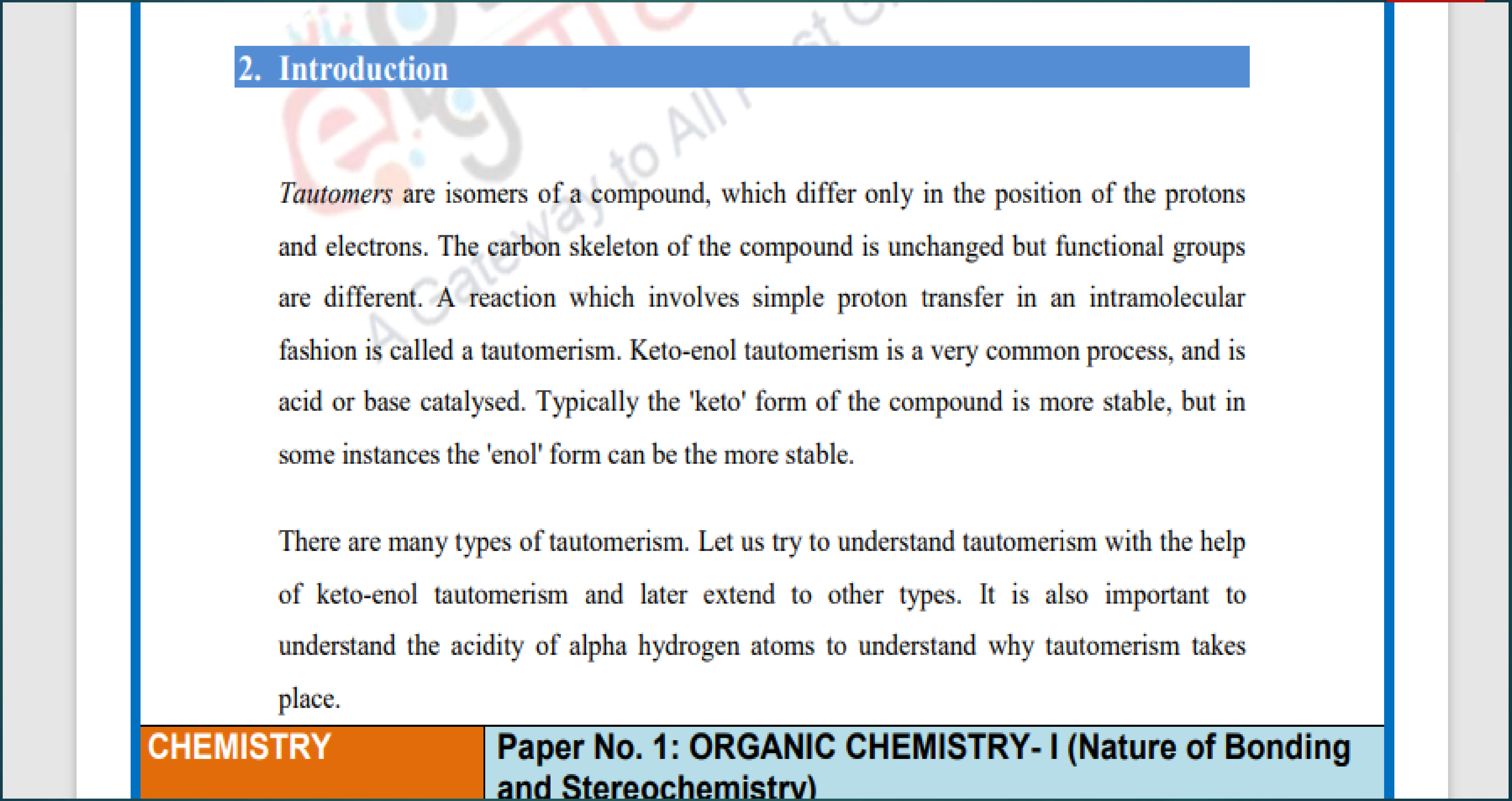
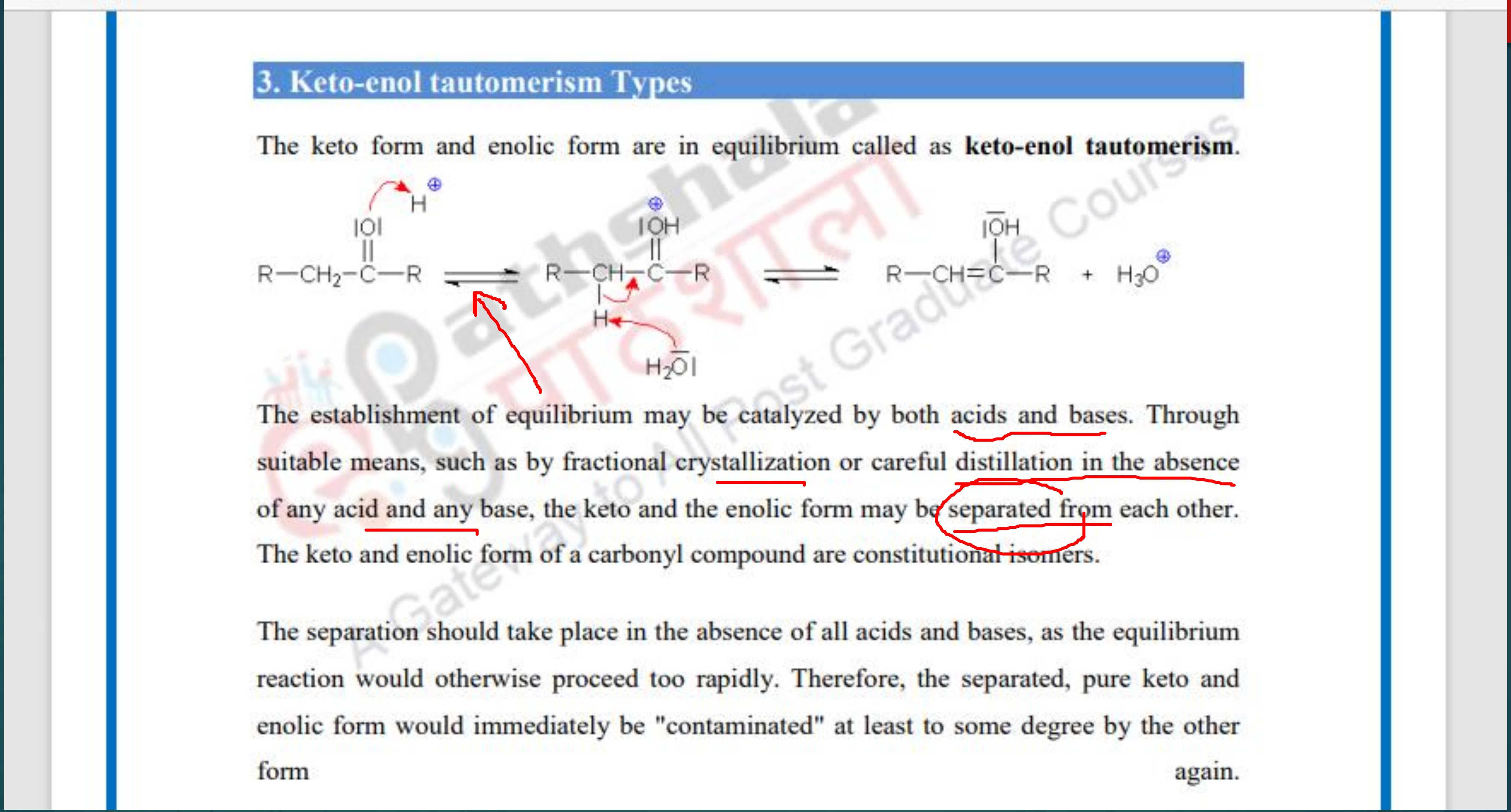
TAUTOMERISM



2. Introduction

Tautomers are isomers of a compound, which differ only in the position of the protons and electrons. The carbon skeleton of the compound is unchanged but functional groups are different. A reaction which involves simple proton transfer in an intramolecular fashion is called a tautomerism. Keto-enol tautomerism is a very common process, and is acid or base catalysed. Typically the 'keto' form of the compound is more stable, but in some instances the 'enol' form can be the more stable.

There are many types of tautomerism. Let us try to understand tautomerism with the help of keto-enol tautomerism and later extend to other types. It is also important to understand the acidity of alpha hydrogen atoms to understand why tautomerism takes place.

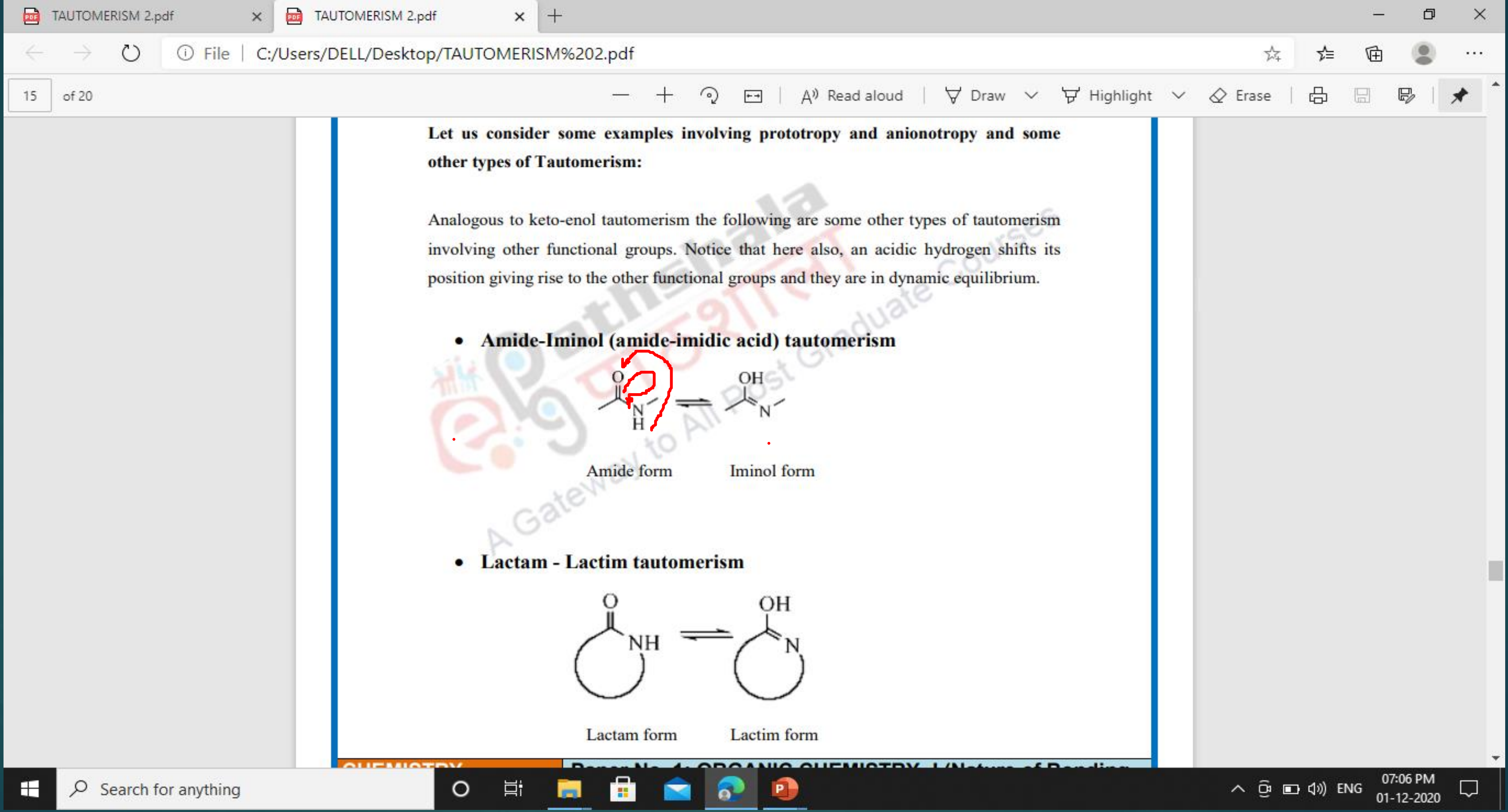


3. Keto-enol tautomerism Types

The keto form and enolic form are in equilibrium called as **keto-enol tautomerism**.

The establishment of equilibrium may be catalyzed by both acids and bases. Through suitable means, such as by fractional crystallization or careful distillation in the absence of any acid and any base, the keto and the enolic form may be separated from each other. The keto and enolic form of a carbonyl compound are constitutional isomers.

The separation should take place in the absence of all acids and bases, as the equilibrium reaction would otherwise proceed too rapidly. Therefore, the separated, pure keto and enolic form would immediately be "contaminated" at least to some degree by the other form again.



Let us consider some examples involving prototropy and anionotropy and some other types of Tautomerism:

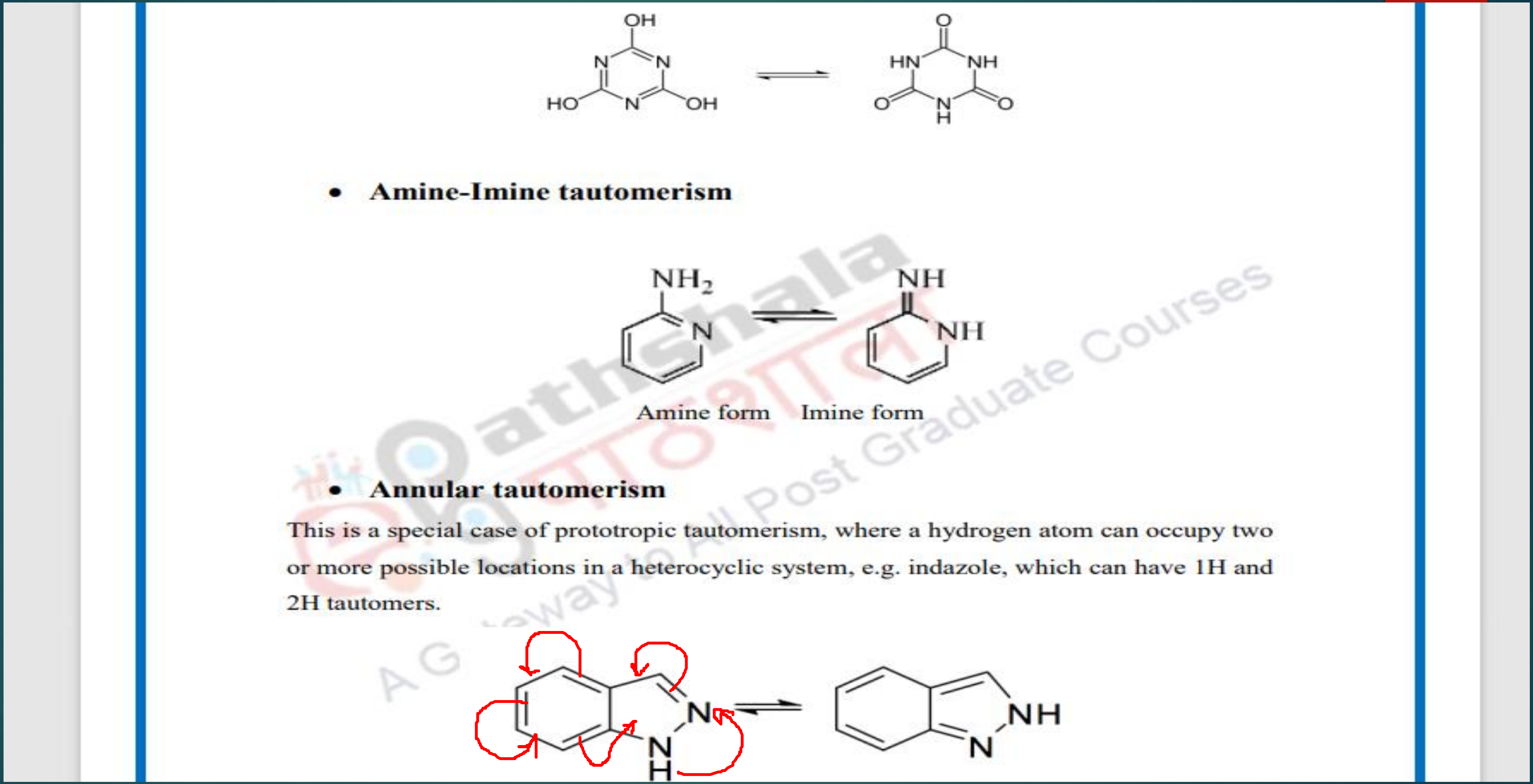
Analogous to keto-enol tautomerism the following are some other types of tautomerism involving other functional groups. Notice that here also, an acidic hydrogen shifts its position giving rise to the other functional groups and they are in dynamic equilibrium.

- **Amide-Iminol (amide-imidic acid) tautomerism**

Amide form Iminol form

- **Lactam - Lactim tautomerism**

Lactam form Lactim form

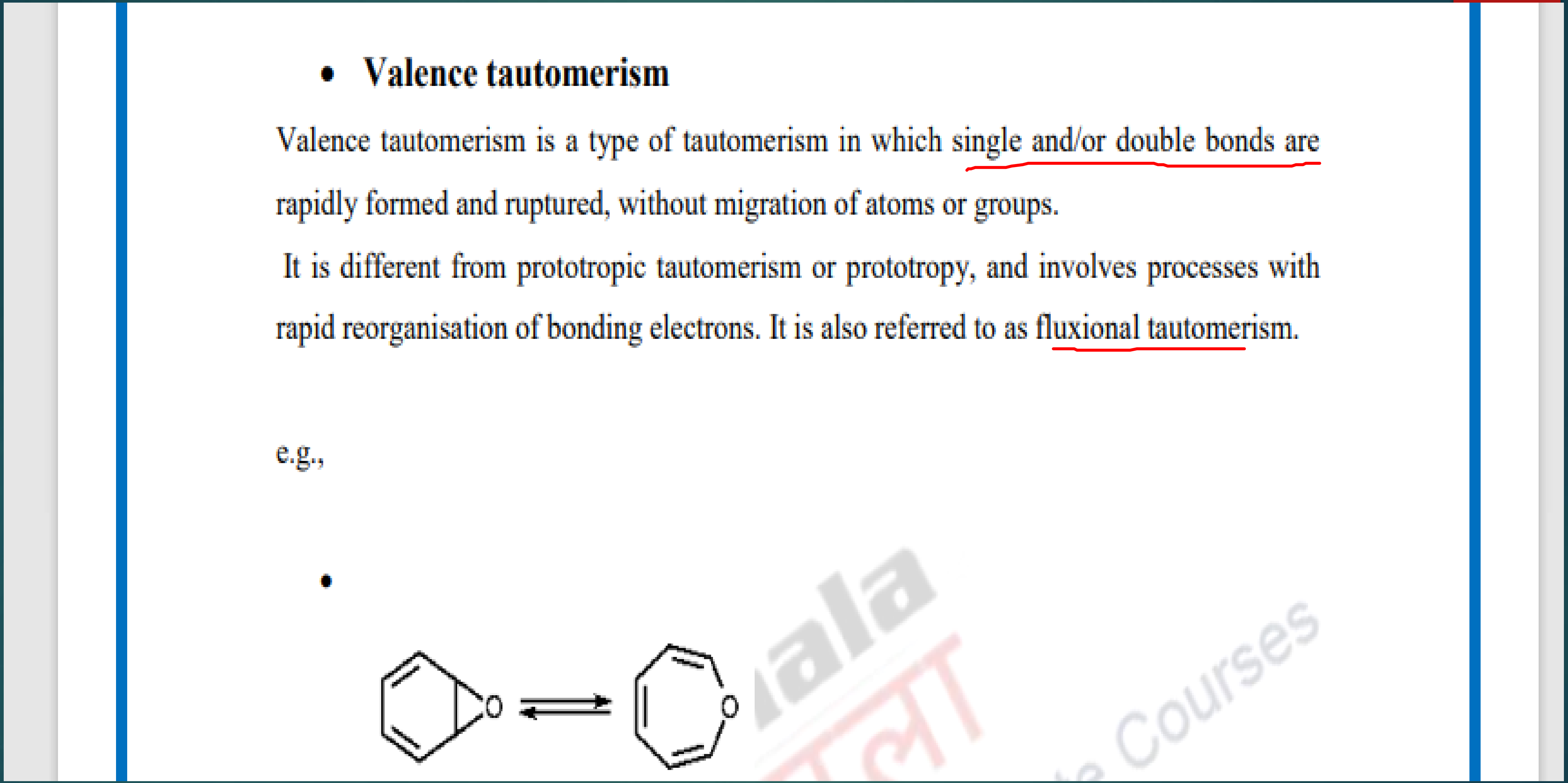


- **Amine-Imine tautomerism**

Amine form Imine form

- **Annular tautomerism**

This is a special case of prototropic tautomerism, where a hydrogen atom can occupy two or more possible locations in a heterocyclic system, e.g. indazole, which can have 1H and 2H tautomers.

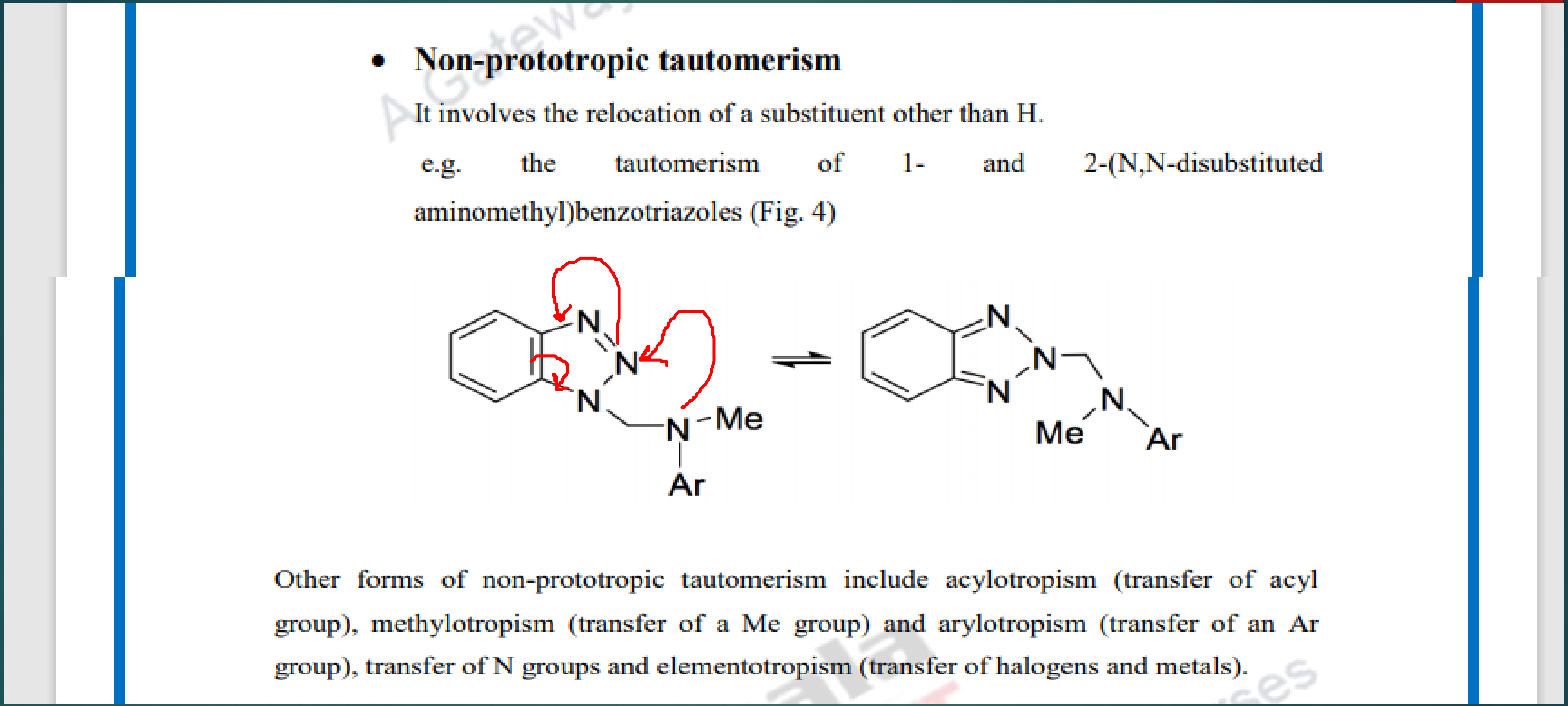


- **Valence tautomerism**

Valence tautomerism is a type of tautomerism in which single and/or double bonds are rapidly formed and ruptured, without migration of atoms or groups.

It is different from prototropic tautomerism or prototropy, and involves processes with rapid reorganisation of bonding electrons. It is also referred to as fluxional tautomerism.

e.g.,

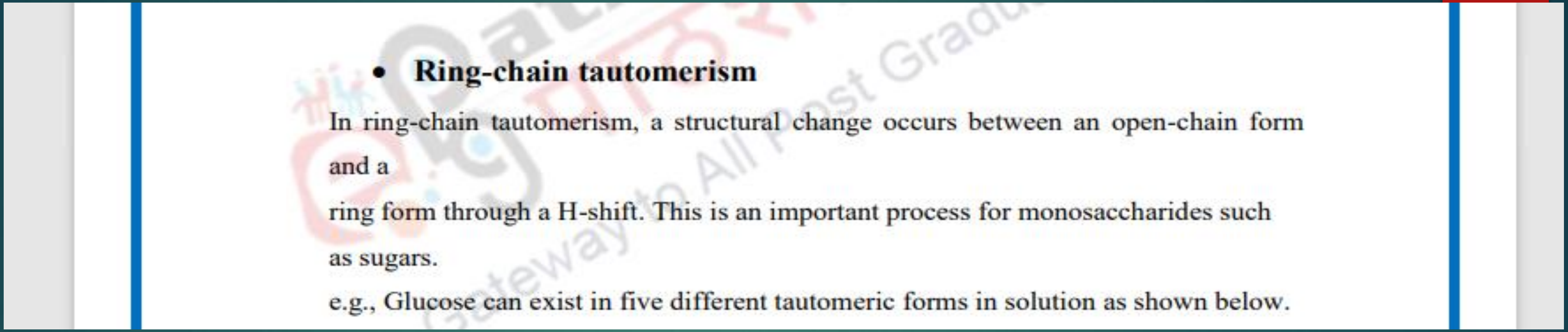


- **Non-prototropic tautomerism**

It involves the relocation of a substituent other than H.

e.g. the tautomerism of 1- and 2-(N,N-disubstituted aminomethyl)benzotriazoles (Fig. 4)

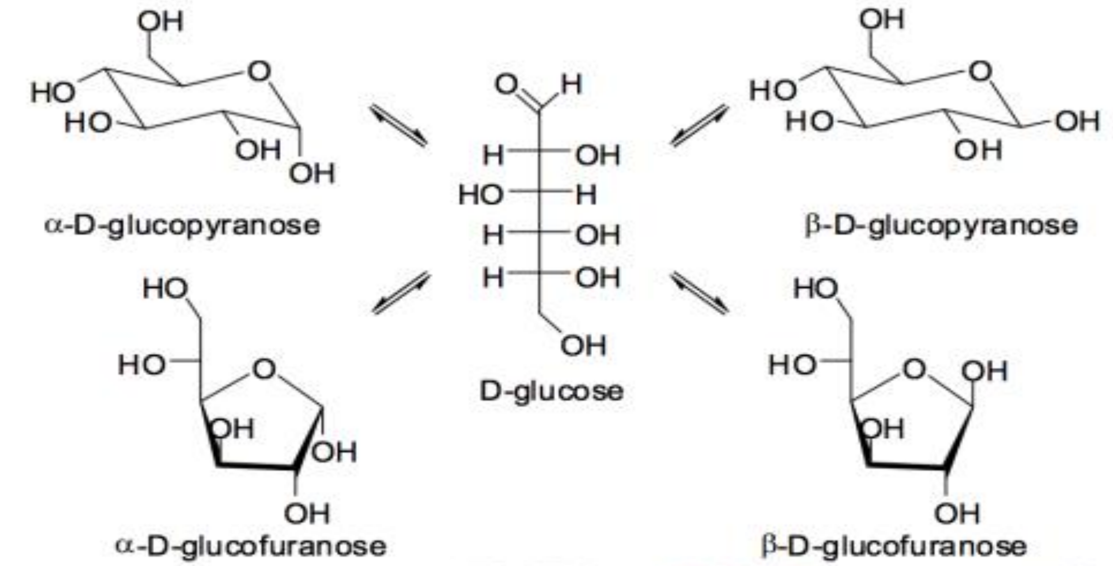
Other forms of non-prototropic tautomerism include acylotropism (transfer of acyl group), methylotropism (transfer of a Me group) and arylotropism (transfer of an Ar group), transfer of N groups and elementotropism (transfer of halogens and metals).



- **Ring-chain tautomerism**

In ring-chain tautomerism, a structural change occurs between an open-chain form and a ring form through a H-shift. This is an important process for monosaccharides such as sugars.

e.g., Glucose can exist in five different tautomeric forms in solution as shown below.



α-D-glucopyranose

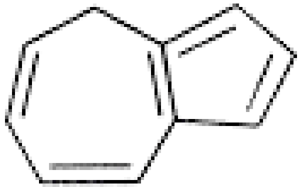
D-glucose

β-D-glucopyranose

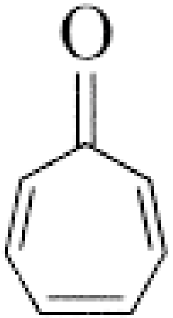
α-D-glucofuranose

β-D-glucofuranose

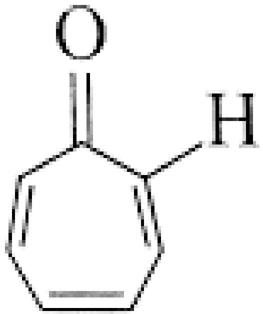
Aromaticity of Benzenoid and Non Benzenoid Compounds



Azulene

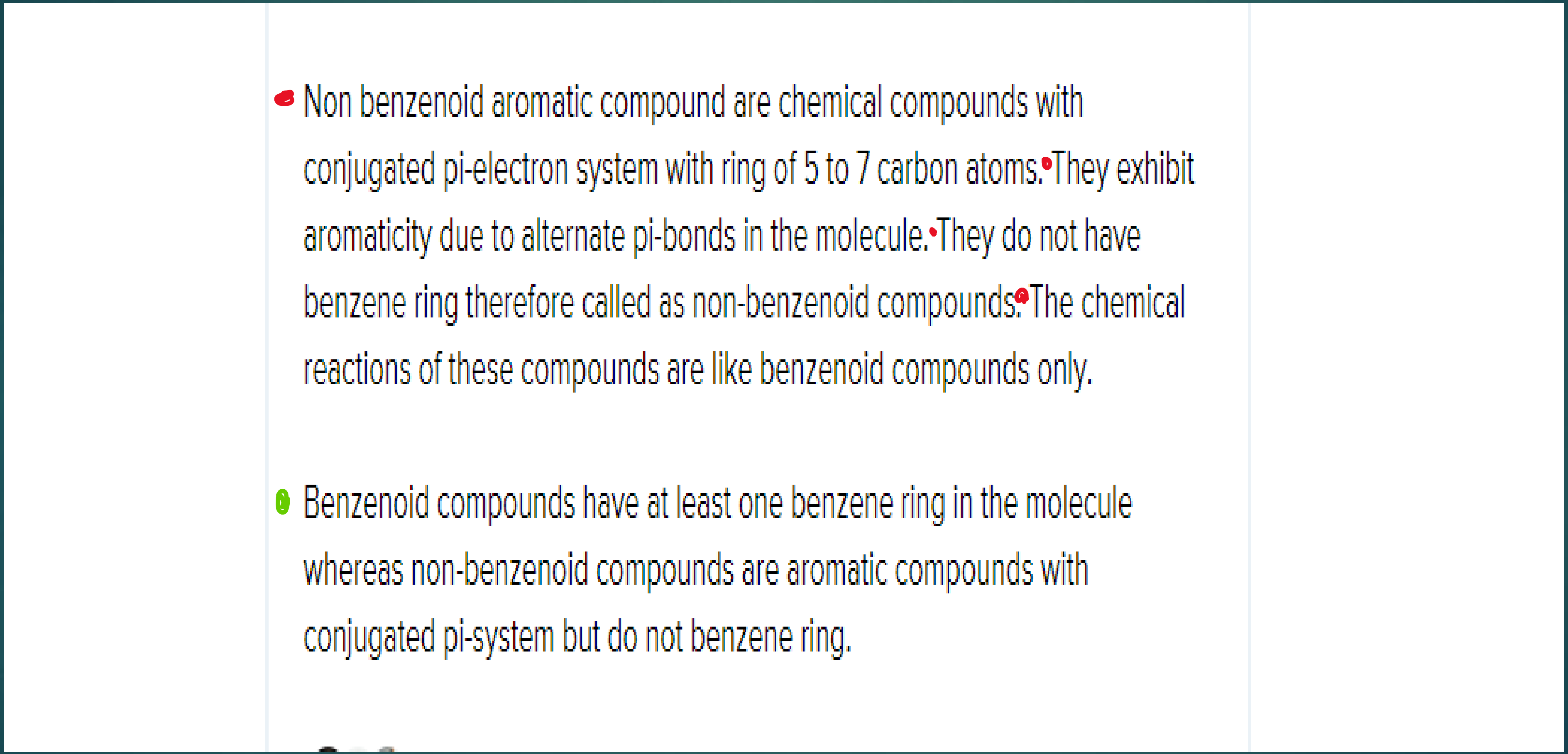


Tropone



Tropolone

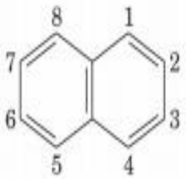
Aromaticity of Benzenoid and Non Benzenoid Compounds



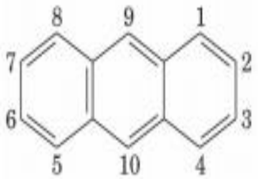
- Non benzenoid aromatic compound are chemical compounds with conjugated pi-electron system with ring of 5 to 7 carbon atoms. They exhibit aromaticity due to alternate pi-bonds in the molecule. They do not have benzene ring therefore called as non-benzenoid compounds. The chemical reactions of these compounds are like benzenoid compounds only.

- Benzenoid compounds have at least one benzene ring in the molecule whereas non-benzenoid compounds are aromatic compounds with conjugated pi-system but do not benzene ring.

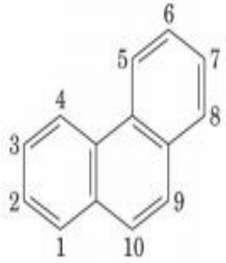
- **Benzenoid Aromatic Compounds**
  - ➔Polycyclic benzenoid aromatic compounds have two or more benzene rings fused together



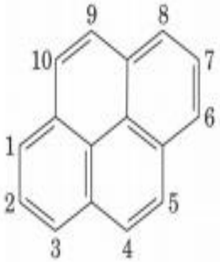
Naphthalene
$C_{10}H_8$



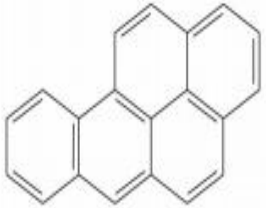
Anthracene
$C_{14}H_{10}$



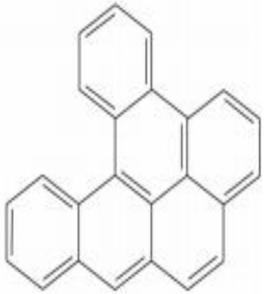
Phenanthrene
$C_{14}H_{10}$



Pyrene
$C_{16}H_{10}$



Benzo[*a*]pyrene
$C_{20}H_{12}$



Dibenzo[*a*,*l*]pyrene
$C_{24}H_{14}$

1. Benzene

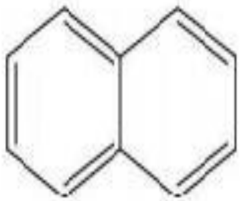
Number of · bonds = 3

Number of · electrons = 6

According to Huckel rule, when n=1, (4n+2) · = (4 X 1 +2) · = 6 · electrons Hence number of · electrons in the compound must be equal to 6

Since Benzene contains 6· electrons, it is aromatic.

2. Naphthalene



Number of · bonds = 5 Number of

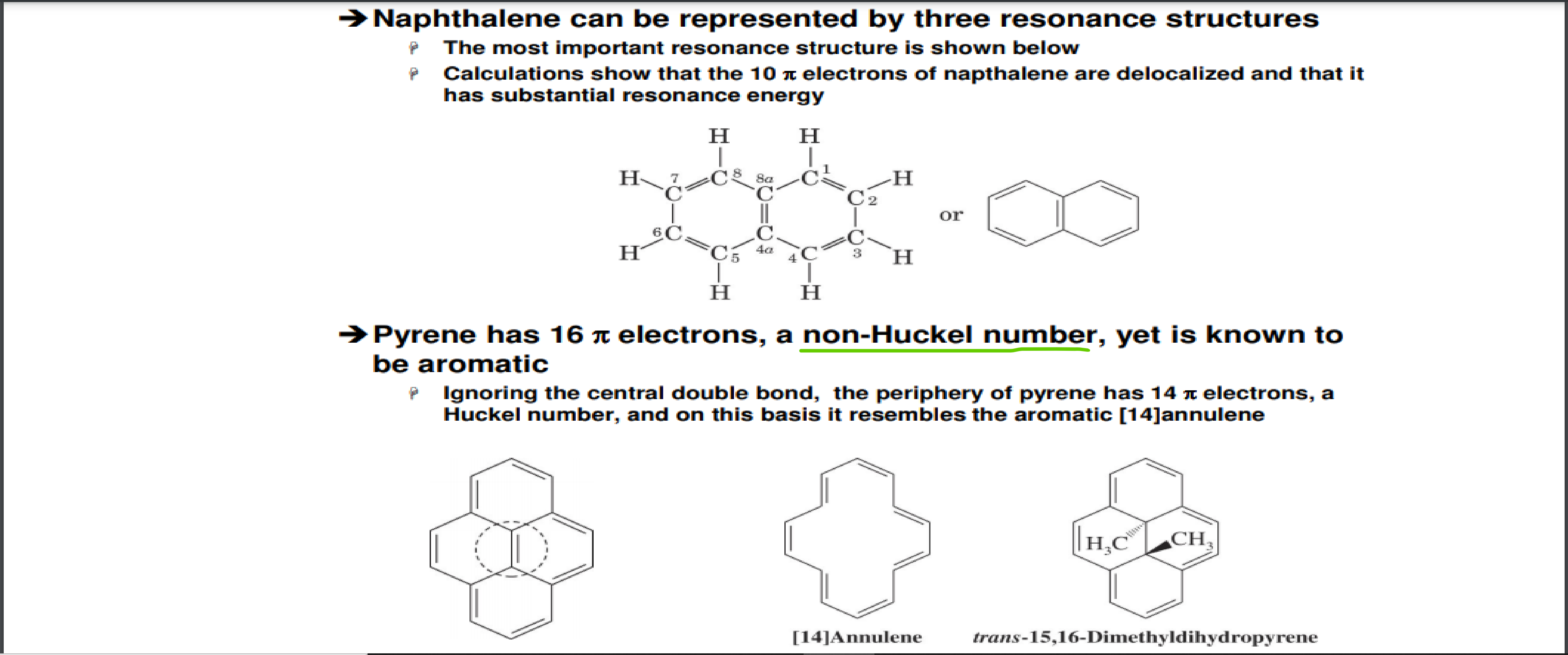
· electrons = 10

According to Huckel rule, when n=2, (4n+2) · = (4 X 2 +2) · = 10 · electrons

Hence number of · electrons in the compound must be equal to 10

Since naphthalene contains 10· electrons, it is aromatic.

Aromaticity of Non benzenoid Compounds



➔ **Naphthalene can be represented by three resonance structures**

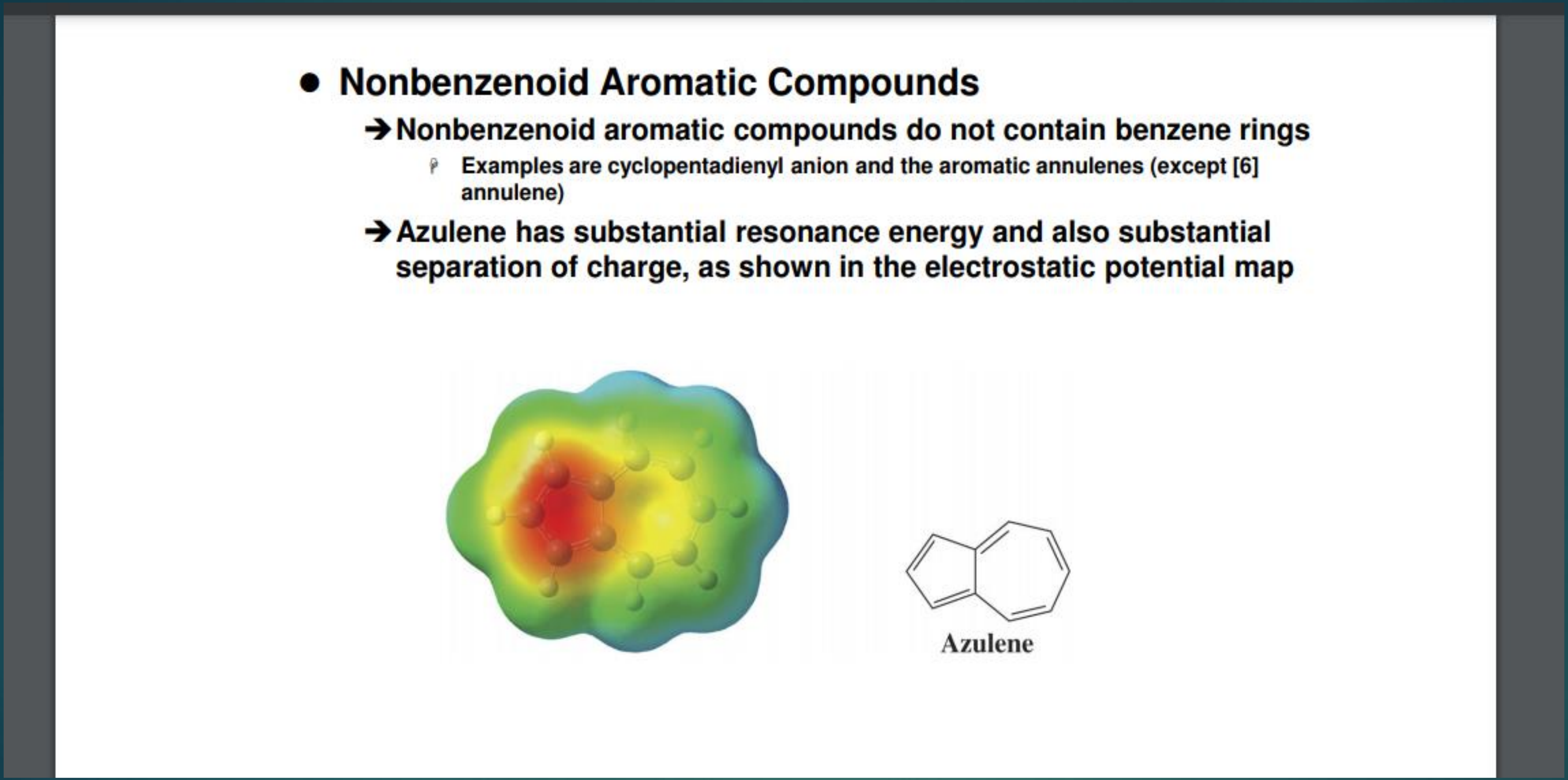
- **The most important resonance structure is shown below**
- **Calculations show that the 10 π electrons of napthalene are delocalized and that it has substantial resonance energy**

➔ **Pyrene has 16 π electrons, a non-Huckel number, yet is known to be aromatic**

- **Ignoring the central double bond, the periphery of pyrene has 14 π electrons, a Huckel number, and on this basis it resembles the aromatic [14]annulene**

[14]Annulene

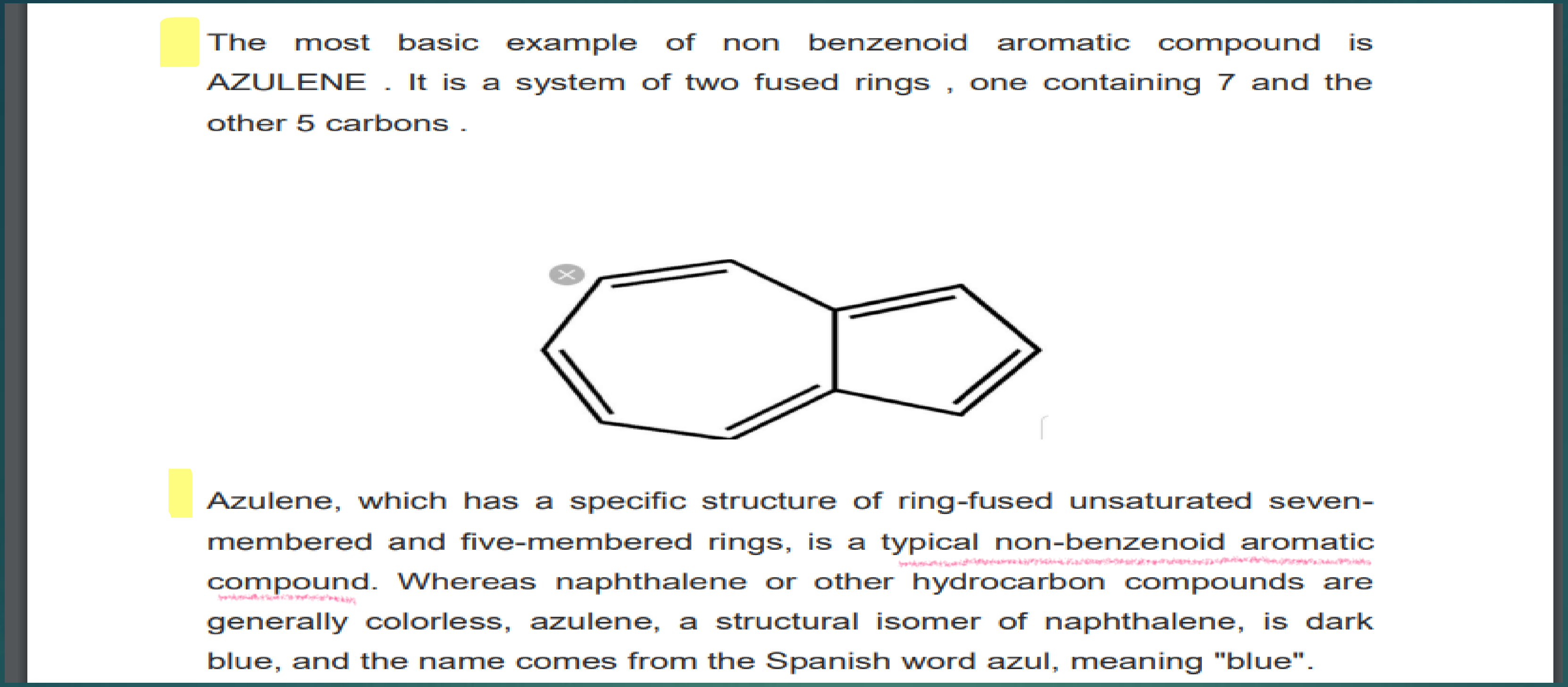
trans-15,16-Dimethyldihydropyrene



Nonbenzenoid Aromatic Compounds

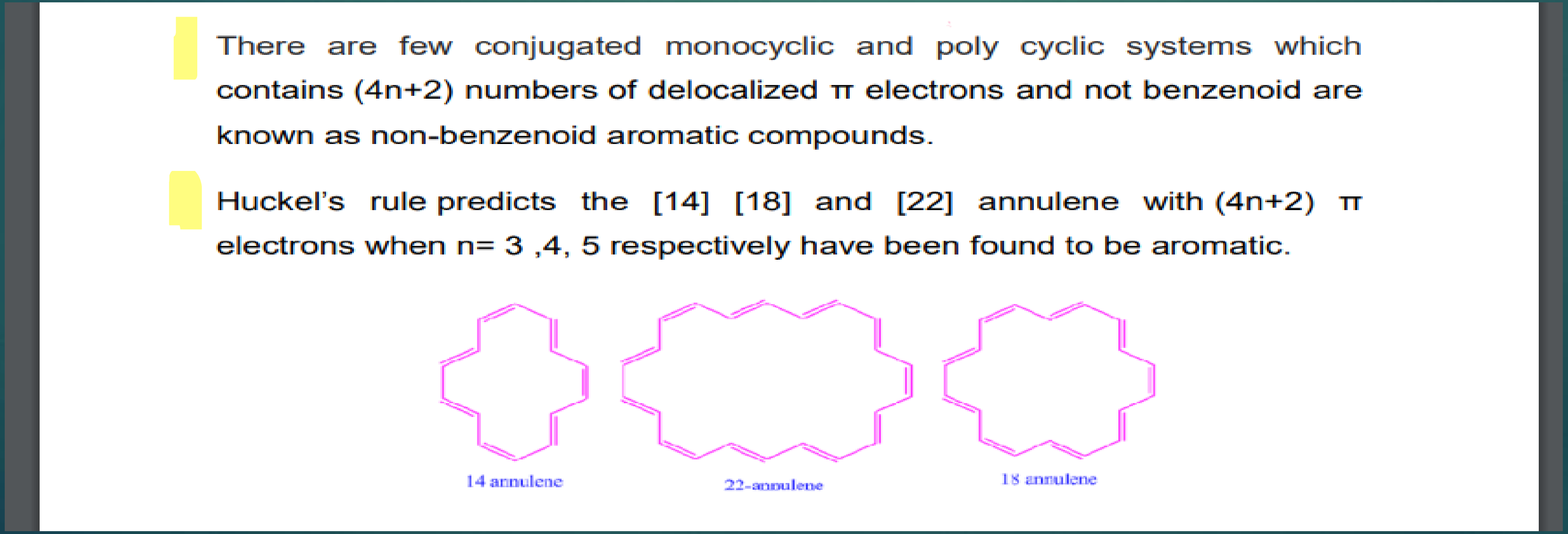
- Nonbenzenoid aromatic compounds do not contain benzene rings
  - Examples are cyclopentadienyl anion and the aromatic annulenes (except [6] annulene)
- Azulene has substantial resonance energy and also substantial separation of charge, as shown in the electrostatic potential map

Azulene



The most basic example of non benzenoid aromatic compound is AZULENE . It is a system of two fused rings , one containing 7 and the other 5 carbons .

Azulene, which has a specific structure of ring-fused unsaturated seven-membered and five-membered rings, is a typical non-benzenoid aromatic compound. Whereas naphthalene or other hydrocarbon compounds are generally colorless, azulene, a structural isomer of naphthalene, is dark blue, and the name comes from the Spanish word azul, meaning "blue".



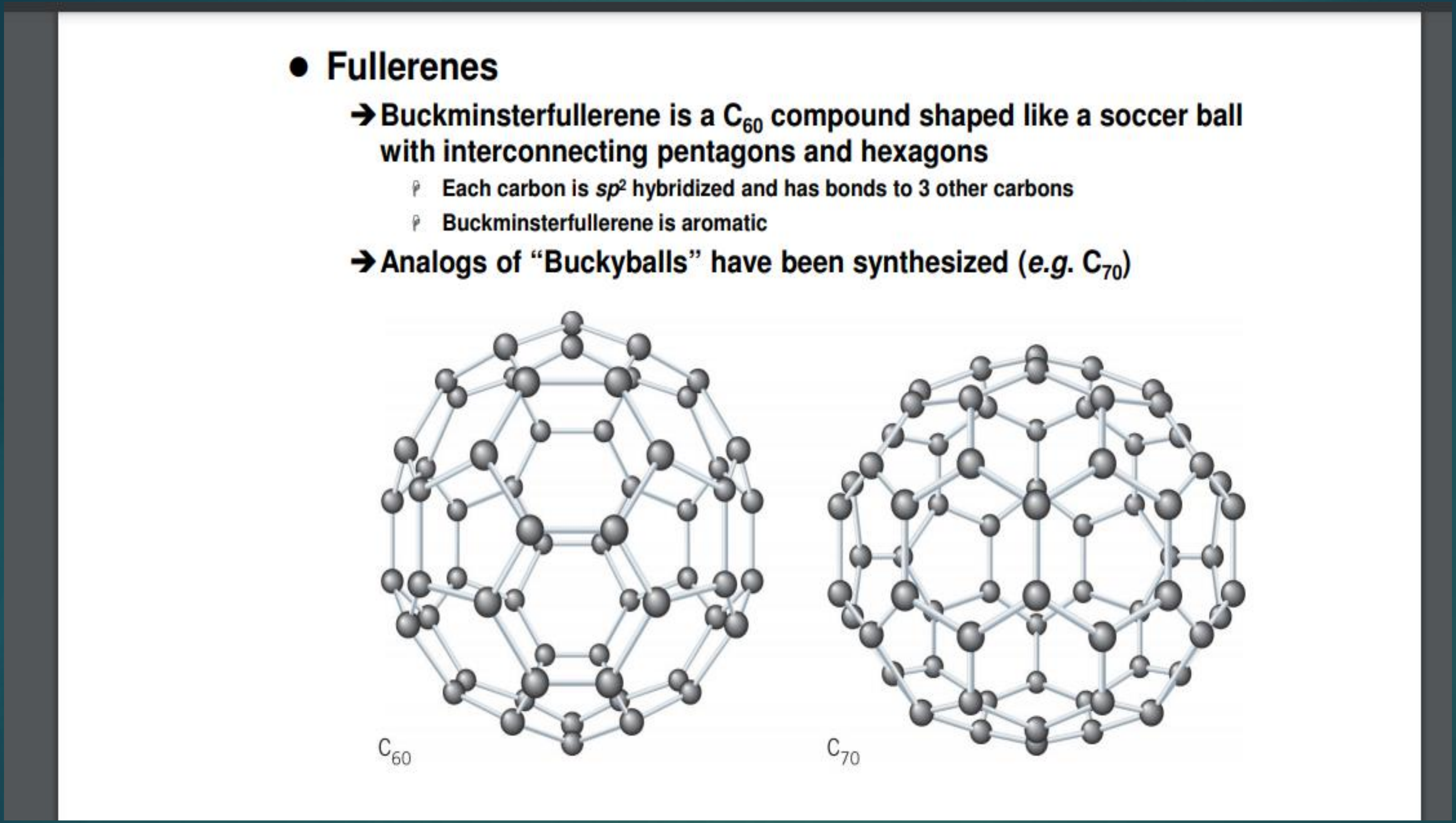
There are few conjugated monocyclic and poly cyclic systems which contains (4n+2) numbers of delocalized π electrons and not benzenoid are known as non-benzenoid aromatic compounds.

Huckel's rule predicts the [14] [18] and [22] annulene with (4n+2) π electrons when n= 3 ,4, 5 respectively have been found to be aromatic.

14 annulene

22-annulene

18 annulene



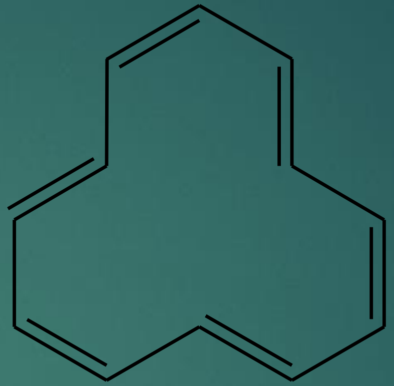
- **Fullerenes**
  - ➔ **Buckminsterfullerene is a C_{60} compound shaped like a soccer ball with interconnecting pentagons and hexagons**
    - **Each carbon is *sp*^{2} hybridized and has bonds to 3 other carbons**
    - **Buckminsterfullerene is aromatic**
  - ➔ **Analogs of “Buckyballs” have been synthesized (*e.g.* C_{70})**

C_{60}

C_{70}

Which of these is aromatic?

A



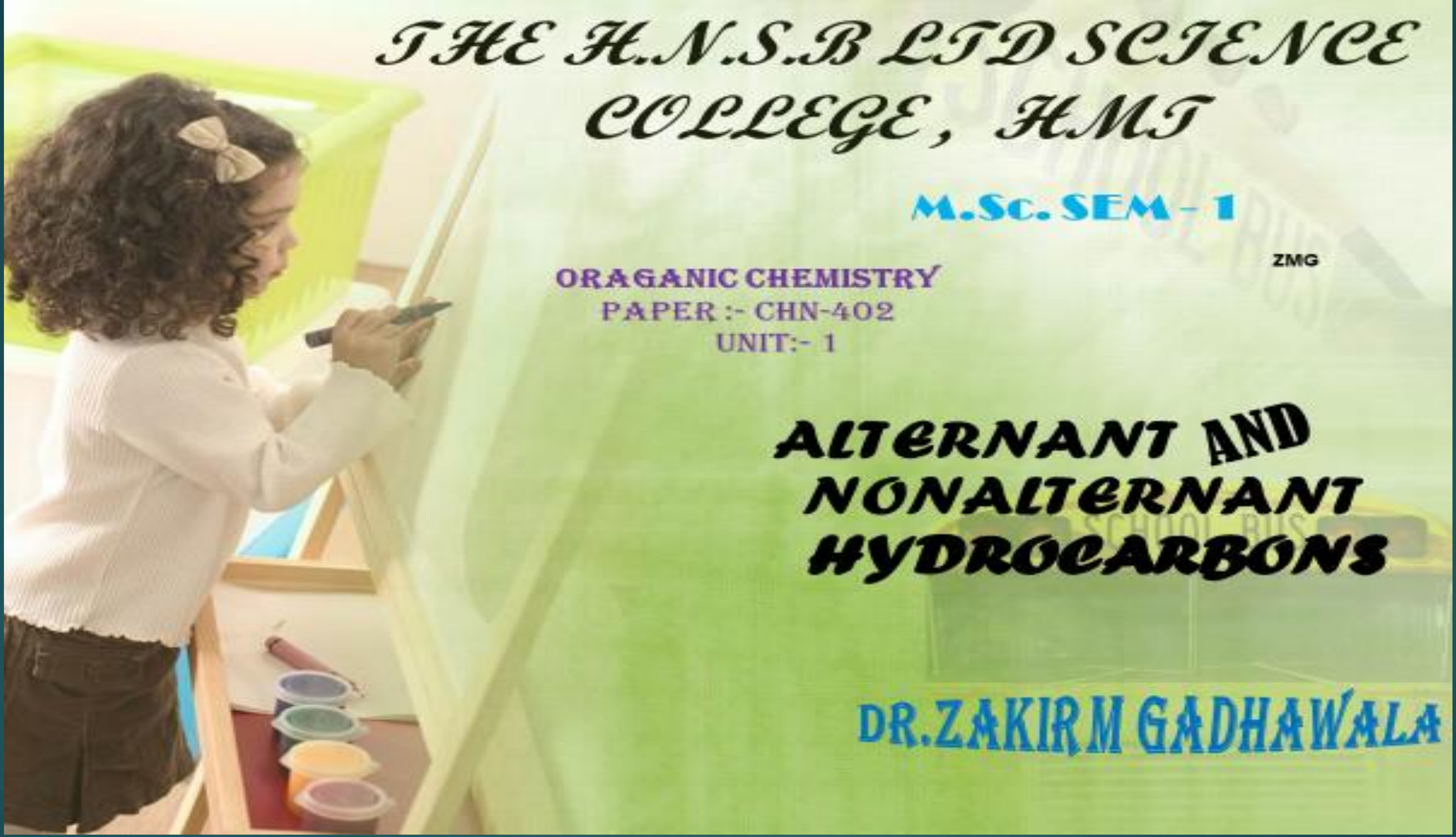
B

A) Is aromatic. Count the number of pi bonds in the outer ring. A has 5 which means 10 pi electrons, 4(2)+2=10. While B has 6 pi bonds and 12 pi electrons, 4(3)=12. Doesn’t meet the Huckel rule requirements for aromaticity.

Is this compound aromatic or antiaromatic?

Antiaromatic – cyclic, planar, conjugated , but does not meet Huckel’s rule.

4 doulbe bonds and 2 triple bonds so 4(2) + 2(4)=16 pi electons. 4n+2 or 4n? 4(4)=16



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M.Sc. SEM - 1

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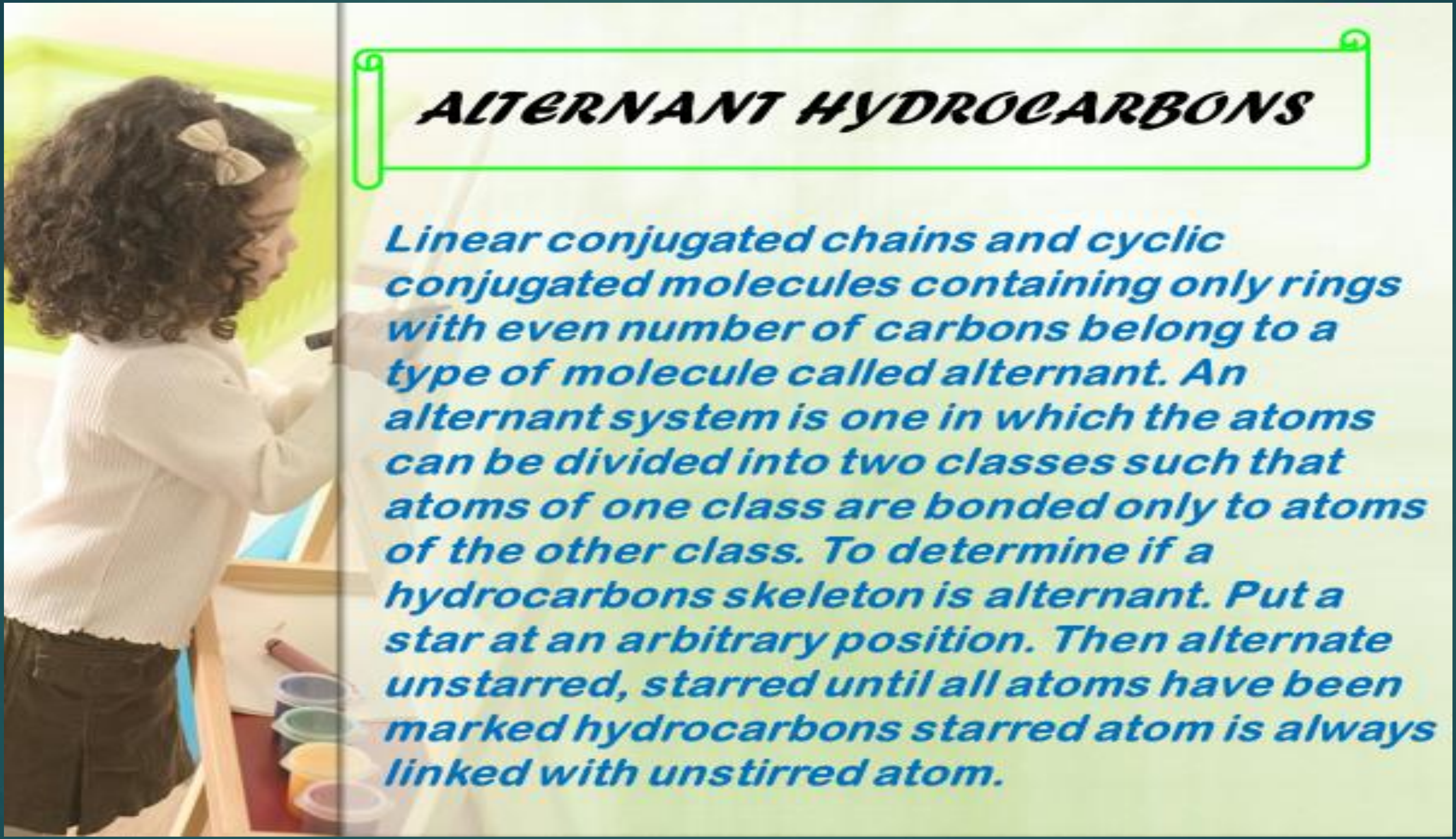
ORAGANIC CHEMISTRY
PAPER :- CHN-402
UNIT:- 1

ALTERNANT AND NONALTERNANT HYDROCARBONS

DR.ZAKIR M GADHAWALA



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 hydrocarbons starred atom is always linked with unstirred atom.

ALTERNANT HYDROCARBONS ARE OF TWO TYPES:

Even alternant hydrocarbons

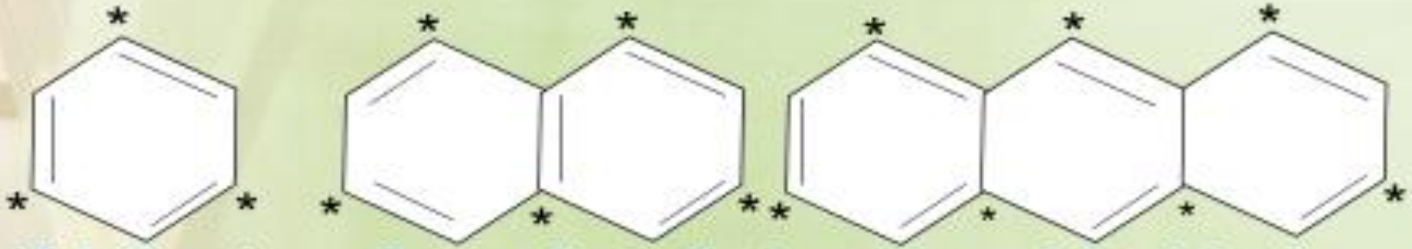
Odd alternant hydrocarbons

EVEN ALTERNANT HYRROCARBONS

Contain even of conjugated atom, i.e., an equal number of starred and unstarred conjugated atom. Examples are 1, 3-butadiene, 1, 3, 5-hexatriene, benzene, naphthalene, anthracene, etc

$$\overset{*}{C}H_2{=}CH{-}\overset{*}{C}H{=}CH_2$$

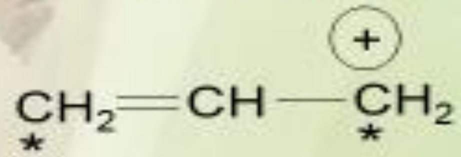
$$\overset{*}{C}H_2{=}CH{-}\overset{*}{C}H{=}CH{-}\overset{*}{C}H{=}CH_2$$

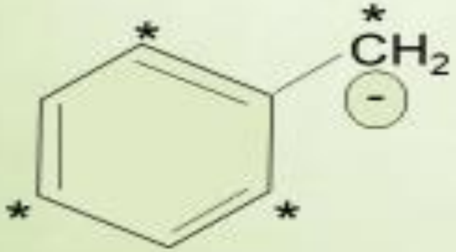


Aliphatic and aromatic even alternant hydrocarbons contain only two types of molecular orbitals, bonding and antibonding. Numbers of bonding molecular orbitals are always equal to the number of antibonding molecular orbitals. In even alternant hydrocarbons all the bonding molecular orbitals are filled and pi-electrons are uniformly spread oven the unsaturated atoms.

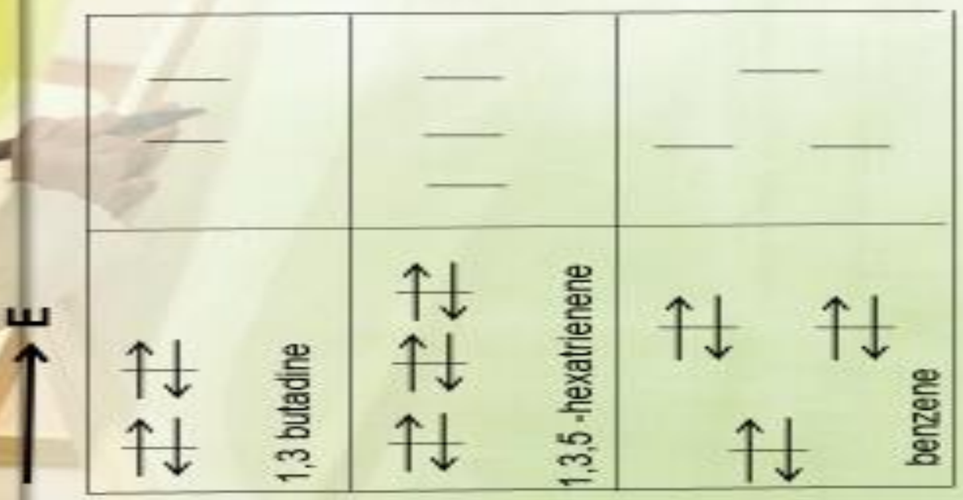
ODD ALTERNANT HYDROCARBONS

Contation 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 are not the same.

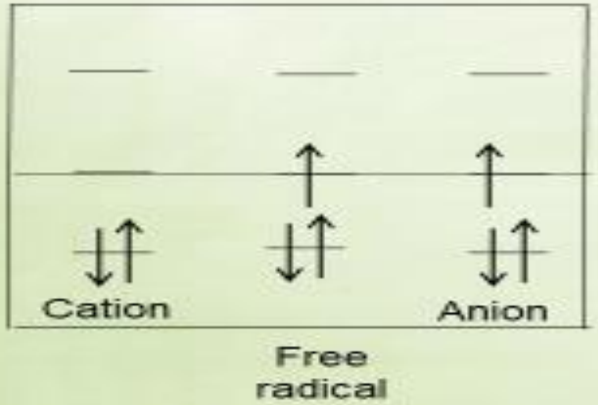




Odd alternant hydrocarbons contain three types of molecular orbital: bonding, antibonding and non-bonding molecular orbital. Bonding molecular orbitals are equals to the antibonding molecular orbitals.



Energy levels in even alternant hydrocarbons.

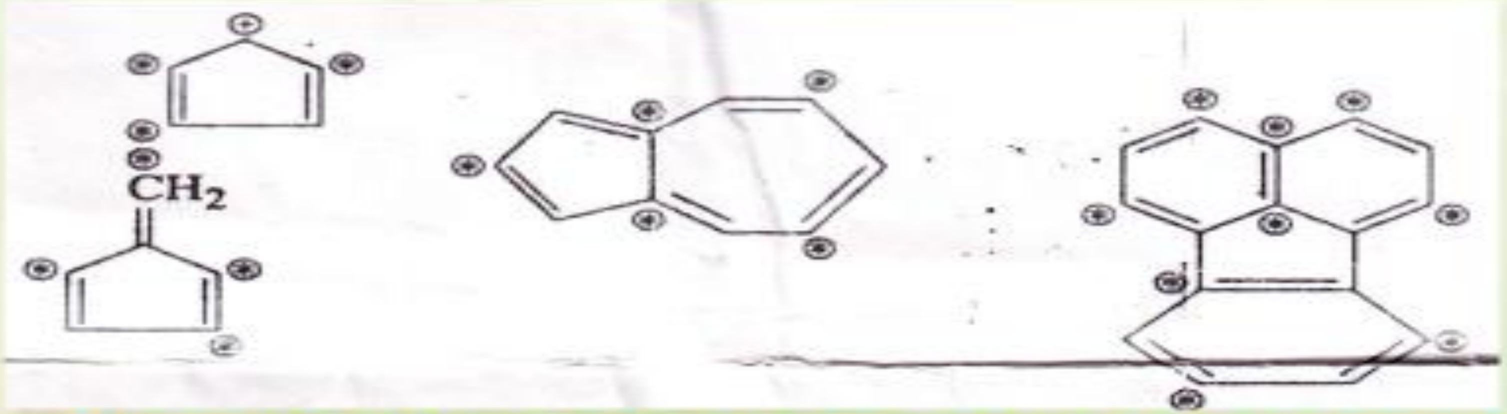


Energy levels in odd (allyl systems) alternant hydrocarbons.

NON-ALTERNANT HYDROCARBONS

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

Examples



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

REFERENCES

- *ADVANCED ORAGANIC CHEMISTRY*

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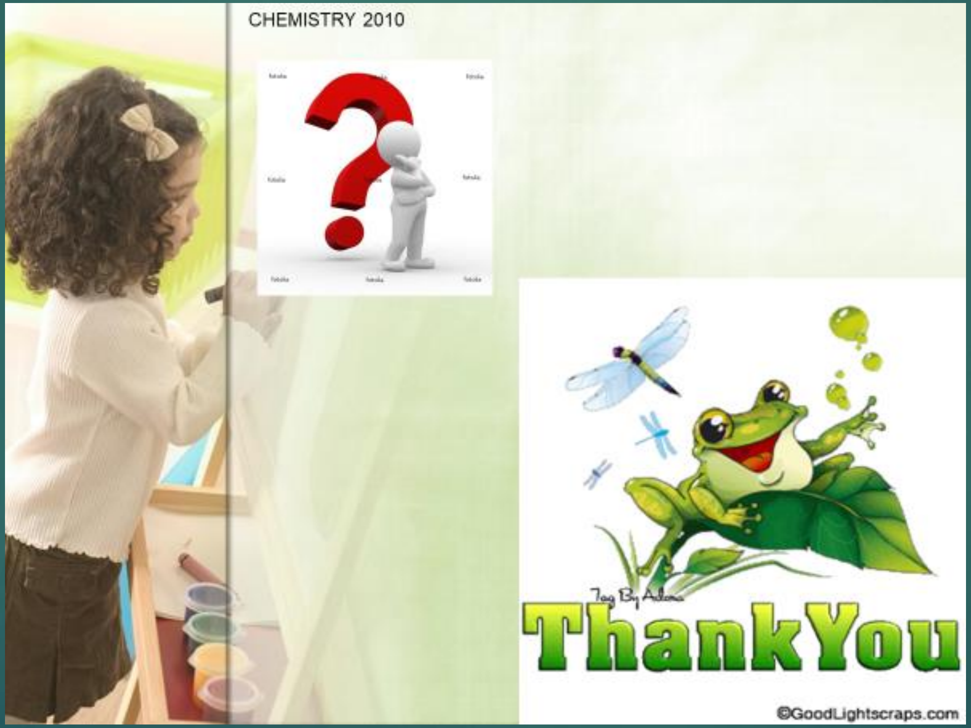
AUTHOR :- Dr. JAGDAMBA SINGH
Dr. L.T.S YADAV

Dr. Z. M. Gadhawala



CHEMISTRY 2010