Hammett Equation Problems

* The Substituent Constant (σ) :

$$\sigma = \log \left(\frac{K_x \, C_6H_4COOH}{K_H \, C_6H_5COOH} \right)$$

where x is substituent

$$\sigma = pK_a(H) - pK_a(x)$$

- It is a logarithm of the ratio of the ionisation Constant of the Substituted benzoic acid to the ionisation Const. of unsubstituted benzoic acid.

ex

$\sigma_m - OH\,C_6H_4COOH$ is calculated as

$$\sigma_m = \log \left(\frac{K_{OH}\, C_6H_4COOH}{K_H \, C_6H_4COOH} \right)$$

$K_x = 8.3 \times 10^{-5}$, $K_H = 6.3 \times 10^{-5}$

$$\sigma = \log \left(\frac{8.3 \times \cancel{10^{-5}}}{6.3 \times \cancel{10^{-5}}} \right)$$

$$= \log 8.3 - \log 6.3$$

$$= 0.9191 - 0.7963$$

$$= 0.1198 \approx 0.12$$

→ σ value is a measure of the total polar effect I & R of a substituents on the rea^n centre i.e. it represents the ability of substituent to withdraw or donate electrons by the Combination of the inductive & resonance effects of the substituents.

- The two effect may work in same direction or in the opposite direction.
- For Some substituents, σ value ~~&~~ at m- position differs from that for the substituent at para position.

ex - The σ - value for m-OH group is +0.12 while that for P-OH group is -0.37.

① σ value may be negative or positive number. A -ve value for a group at a particular positions m or P- indicates its greater e$^{\ominus}$ donating ability to the rea^{n} centre than H, where as a possible value for a substituent tells us that the substituent is more e$^{\ominus}$ withdrawing than H.

The more the -ve value of a group, the more is the e$^{\ominus}$ donating ability while the more the +ve value the more is its electron withdrawing character.

② In some case, the two values bear the same sign while in some other cases they have diff. signs, they have identical signs when the I & R effects work in one & same direction if the signs are different, the two effects are working in the opposite directions.

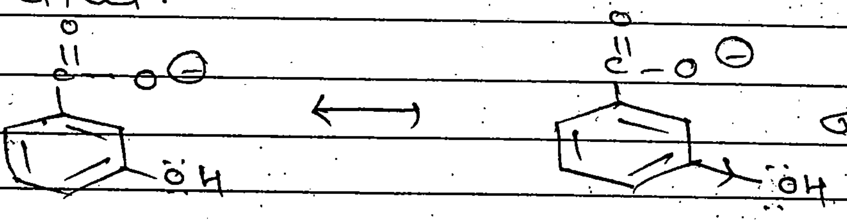
for ex -

- OH group has -ve σ_p value but +ve σ_m value since a group at m-position can not take part in the delocalisation of is or charge OH group exerts -I effect when it is at m-position with respect to the rea^{n} centre because of this -I effect.

-ve $\sigma_p \longrightarrow -0.37$

+ve $\sigma_m \longrightarrow +0.12$

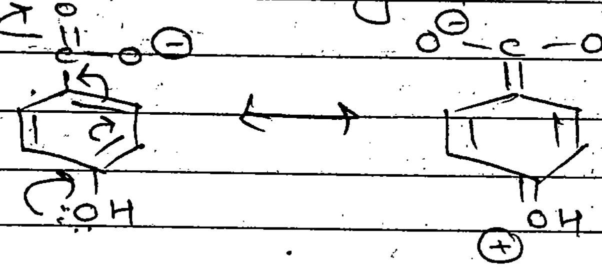
- OH group has a positive σ value on the other hand P-OH group has a -ve σ value which indicates that it donates e$^{\ominus}$ to the rea^{n} centre i.e. It activates the ring by +R effect in this case the -I effect of OH group is less than the +R effect.



$\sigma = +0.12$

-I effect

Here at m-position instead of delocalisation -I effect takes place because of electronegativit different & another reason is that active rea^{n} (centre or not taking part in delocalisation



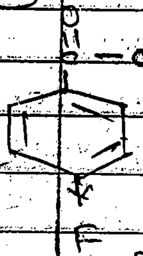
$\sigma_p = -0.37$

+R effect.

Q: Comment on the diff. in the σ value of following substituent.

① $\sigma_{p-F} = 0.06$ ② $\sigma_{m-F} = 0.34$

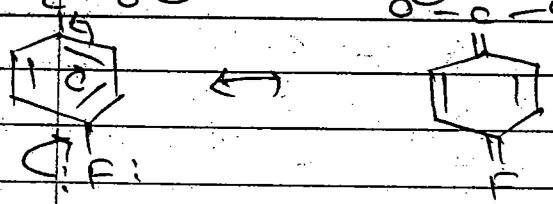
①



Here F is e$^{\ominus}$ withdrawing group (-I effect at para position.

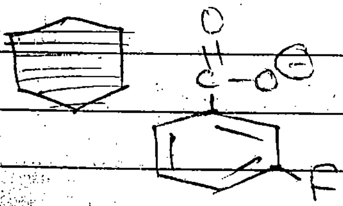
Hence ~~No~~ σ value is +ve (0.06)

But some mesomeric effect also occurs



∴ σ_{p-F} value is less as Compare to σ_{m-F}

② σ_m-F:



Here only -I effect is oppeeating mesomeric effect is absent.

Hence σ_m value is more

Q: Estimate the sigma value for P-OH, P-CF$_3$ & m-C$_6$H$_5$- groups.

Given that	Pka
① Benzoic acid	4.20
② P-hydroxy B.A	4.57
③ P-triflu㎚ methyl (CF$_3$) B.A	3.77
④ m-phenyl B.A	4.26

$\sigma = P_{KH} - P_{Kx}$

$\sigma P\text{-OH} = 4.20 - 4.57 = -0.37$

$\sigma P\text{-CF}_3 = 4.20 - 3.77 = 0.43$

$\sigma m\text{-C}_6H_5 = 4.20 - 4.26 = -0.06$

⑤ ~~P-NO$_2$~~ ⟶ . .

~~Q. pKa values of P-NO$_2$ B.A, P-ome B.A~~

Q. Pka values of P-Nitrobenzoic acid, P-methoxy benzoic acid, m-chlorobenzoic acid & benzoid acid are 3.44, 4.47, 3.83 & 4.20 respectively calculate σp-NO$_2$, σp-ome, σm-cl.

Given: $P_{KH} = 4.20$, $P_{K NO_2} = 3.44$, $P_{K ome} = 4.47$, $P_{K cl} = 3.83$

$\sigma = P_{KH} - P_{Kx}$

$\sigma P\text{-NO}_2 = 4.20 - 3.44 = 0.76$

$\sigma m\text{-cl} = 4.20 - 3.83 = 0.37$

$\sigma p\text{-ome} = 4.20 - 4.47 = -0.27$

Q. Estimate σm-ome & σp-cl from the following data Pka of benzoic acid, m-ome & P-cl are 4.20, 3.08 & 3.99 respectively

P_{ka} B.A → 4.20

P_{ka} m-ome → 3.08

P_{ka} p-cl B.A → 3.99

$$\sigma = P_{KH} - P_{Kx}$$

$\sigma_{m-ome} = 4.20 - 3.08 = 1.12$

$\sigma_{p-cl} = 4.20 - 3.99 = 0.21$

Q : Derive the Hammett eqⁿ & calculate the Substituent Const. of the following ethyl benzoate

Given data :

P_{KH} (unsubstituted ethyl benzoate) = 4.20

P_{ka} m-me = 4.26

P_{ka} p-H = 4.20

P_{ka} m-NO_2 = 3.49

P_{ka} p-ome = 4.47

P_{ka} m-Br = 3.80

$$\sigma = P_{KH} - P_{Kx}$$

$\sigma_{m-me} = 4.20 - 4.26 = -0.06$

$\sigma_{p-H} = 4.20 - 4.20 = 0$

$\sigma_{m-NO_2} = 4.20 - 3.49 = 0.71$

$\sigma_{p-ome} = 4.20 - 4.47 = -0.27$

$\sigma_{m-Br} = 4.20 - 3.80 = 0.4$

Substituent Constant σ

Sr. No.	Substituent	σm	σp
1	$O^{\ominus}$	−0.7	−0.8
2	NH_2	−0.16	−0.66
3	CMe_3	−0.10	−0.20
4	NMe_2	−0.10	−0.63
5	me	−0.07	−0.17
6	Ethyl	−0.04	−0.15
7	$Si(CH_3)_3$	−0.04	−0.07
8	H	0.0	0.0
9	C_6H_5	0.06	−001
10	ome	0.12	−0.27
11	OH	0.12	−0.37
12	Sme	0.15	0.0
13	F	0.34	0.06
14	Cl	0.37	0.23
15	Br	0.39	0.23
16	I	0.35	0.28
17	COOH	0.35	0.44
18	COOR	0.35	0.44
19	$\overset{O}{\overset{\|}{C}}-me$	0.38	0.50
20	CF_3	0.43	0.54
21	CN	0.56	0.66
22	$^{\oplus}NH_3$	0.60	0.86
23	SO_2me	0.64	0.73
24	NO_2	0.71	0.78
25	$^{\oplus}NMe_3$	0.88	0.82
26	$^{\oplus}N\equiv N$	1.65	1.91

★ Delocalised chemical bonding :

- Although the bonding of many Comp. can be adequately described by a single lewis structure, this is not sufficient for many other Compounds.
- These Comp. Contain one or more bonding orbital that are not restricted to two ~~or~~ atoms, but that are ~~seperated~~ spread out over three or more such bonding is said to be delocalised.

Conjugation :

- The heat of hydrogenation of a terminal alkene is about -30 kcal/mol as in the case of 1-butene.
- A Comp. with two non-interacting terminal double bonds should be about twice this value (-60 kcal/mol)
- This is found to be in case of 1,4-pentadiene ($\Delta H^\circ = -60.5$ kcal/mo).
- However, ~~the~~ on hydrogenation of a Conjugated diene eg. 1,3-butadiene generates less energy. The diff. in energy is about 3.6 kcal/mol, is a result of stabilizing interaction betⁿ two double bonds & is called resonance energy of 1,3-butadiene.

$$H_2C=CH-CH_2-CH_3 \xrightarrow{H_2, Pt} CH_3-CH_2-CH_2-CH_3$$

$$\Delta H^\circ = -30.1\ \text{kcal/mol}$$

$$H_2C=CH-CH_2-CH=CH_2 \xrightarrow{H_2, Pt} CH_3-CH_2-CH_2-CH_2-CH_3$$

$$\Delta H^\circ = -60.2\ \text{kcal/mol}$$

$$H_2C=CH-CH=CH_2 \xrightarrow{H_2, Pt} CH_3-CH_2-CH_2-CH_3$$

$$\Delta H^\circ = -\cancel{5}56.6\ \text{kcal/mol.}$$

Resonance energy of 1,3-butadiene = 60.2 kcal - 56.6
= 3.6 kcal/mol.

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- The stability of Conjugated diene depends on two factors. Firstly it is the hybridization of the orbital Forming the single bond.
- The single bond in butadiene is Formed due to the overlap of an sp^2 orbital With another orbital, While the single bond formed in 1,4-pentadiene result from the overlap of an sp^3 orbital With an sp^2 orbital.
- As an average the 2s orbital $e^\ominus$ is closee to the nucleus than a 2p electron, the electrons in an sp^2 orbital (With 33.3 % s charactee) are closee to the nucleus than a ~~2p electron~~, ~~the electrons~~ sp^3 orbital (With 25 % s character).
- The length of bond depends on the closeness of electrons in the bonding orbital to the nucleus.
- Thus, the more the s character in the orbitals Forming the σ bond, the shorter is the bond
- This means that a σ bond Formed by an sp^2-sp^2 overlap is shorter than a σ bond formed by an sp^3 - sp^2 overlap.
- Shorter bonds are more stable, therefore, the molecule is more stable.

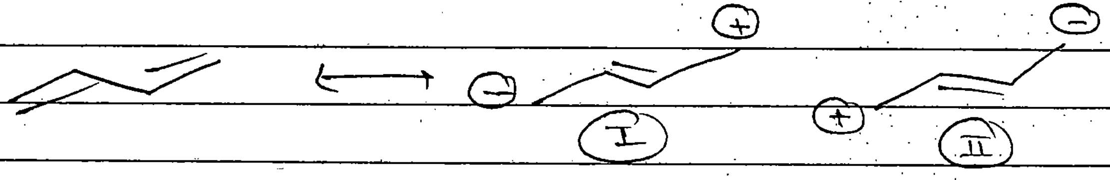
$H_2C = CH - CH = CH_2$ $H_2C = CH - CH_2 - CH = CH_2$

σ bond by sp^2-sp^2 σ bond by sp^3-sp^2 overlap

1,3 - Butadiene   1,4 - pentadiene

- Secondly Conjugated diene is more stable than an isolated diene due to resonance Which means that the Comp. had delocalized $e^\ominus$.
- The π $e^\ominus$ in a Conjugated double bonds are not localised betn two carbons, but instead over four Carbons.

- As a Consequence of resonance the single bond in 1,3-butadiene is not a pure single bond & has a partial double bond character.
- This feature Contributes to that an sp^2-sp^2 bond is shorter & more stable than an sp^2-sp^3 bond.

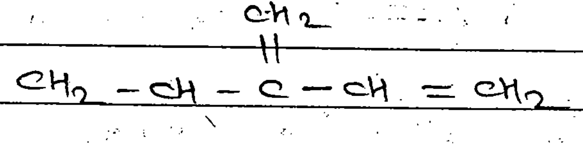


Resonance Forms of 1,3-butadiene.

2) Cross Conjugation :

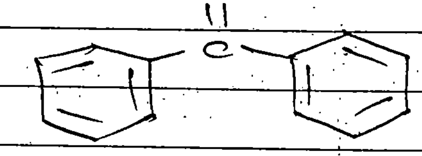
→ Consider a hydrocarbon possessing three double bond two of which are Conjugated to the third but are not Formally Conjugated to each other, this is termed as a cross Conjugated System.

→ In other words a cross Conjugated system has three groups two of which are not conjugated with each other, though each is Conjugated with the third.



$$CH_2-CH-\overset{\overset{CH_2}{||}}{C}-CH=CH_2$$

Polyene



Benzophenone

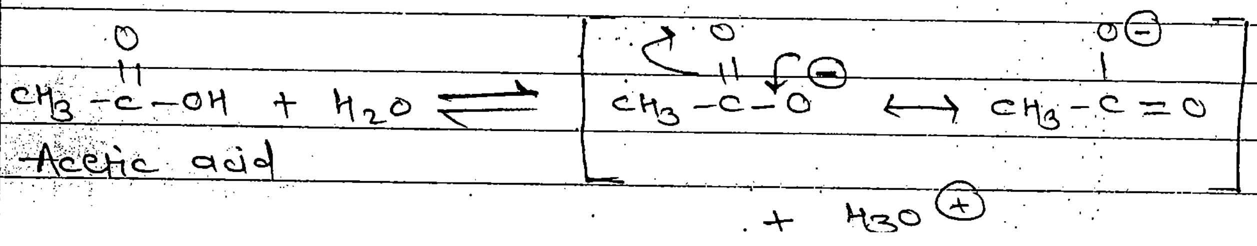
→ Conjugation provides extra Stabilization, however, in the case of Conjugated carboxylic acids or esters this stabilisation is small, Far less smaller than for dienes or unsaturated aldehydes & ketones.

→ one way to explain this behavior is that the Carbonyl group in a Carboxylic function is already involved in Conjugation to an atom with a pair of $e^{\ominus}$ to donate i.e. the oxygen of OH or OR or nitrogen of NH_2.

→ Such a carbonyl group is less able to conjugate with another group.

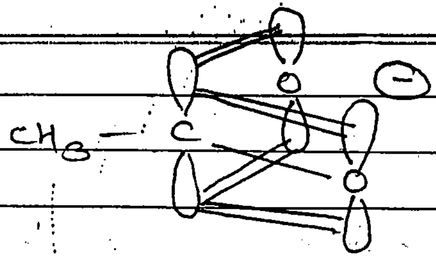
→ This situation is representative of a cross-conjugated System as shown by the π - overlap of P-orbitals

→ Cross Conjugation is less effective than linear Conjugation to stabilise a molecule.

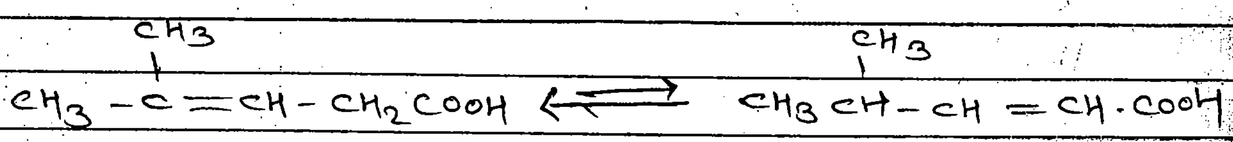


$$CH_3-\overset{\overset{O}{||}}{C}-OH + H_2O \rightleftharpoons \left[CH_3-\overset{\overset{O}{||}}{C}-O^{\ominus} \longleftrightarrow CH_3-\overset{\overset{O^{\ominus}}{|}}{C}=O \right] + H_3O^{\oplus}$$

Acetic acid



— As a further example, 4-methylpent-3-enoic acid, with a trisubstituted double bond, is stabler than 4-methylpent-2-enoic acid, which has a conjugated π-system but has only a disubstituted double bond.



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}=CH-CH_2COOH \rightleftharpoons CH_3\overset{CH_3}{\overset{|}{C}H}-CH=CH\cdot COOH$$

4-Methylpent-3-enoic acid — 4-Methylpent-2-enoic acid

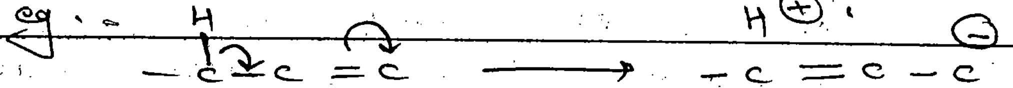
More stable — Less stable

(not Conjugated) — (Conjugated)

Hyperconjugation :

→ Alkyl groups with at least one hydrogen atom on the α- carbon atom, attached to an unsaturated carbon atom are able to release electrons by a mechanism similar to that of electromeric effect.

eg :-



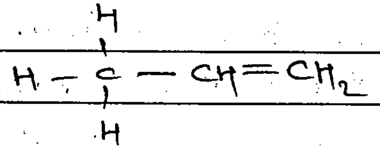
$$-\overset{H}{C}-C=C \longrightarrow \overset{H^{\oplus}}{}-C=C-\overset{\ominus}{C}$$

→ Note that the delocalisation involves σ & π bond orbitals thus it is also known as σ-π Conjugation.

→ This type of $e^{\ominus}$ release due to the presence of the System H-C-C=C is known as hypeeconjugation.

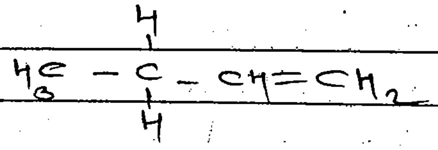
→ Thus more the no. of H-C bonds attached to the unsaturated system more will be the probabili of electron release by this mechanism.

→ The $e^{\ominus}$ release by this mechanism will be greater in methyl (Possessing three hypeeconjugated H-C bonds), less in ethyl having two such bonds & iso-propyl have one C-H bond and again essentially zero in tert. butyl hypeeconjugated H-C bonds.



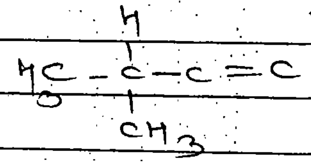
$$H-\underset{H}{\overset{H}{C}}-CH=CH_2$$

Methyl
(3H-C hypee
Conjugated bonds)



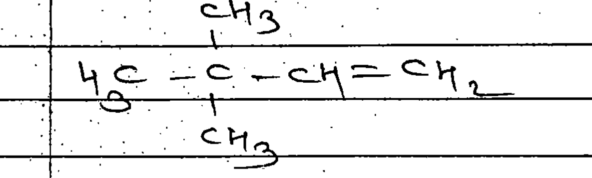
$$H_3C-\underset{H}{\overset{H}{C}}-CH=CH_2$$

Ethyl
(2H-C)



$$H_3C-\underset{CH_3}{\overset{H}{C}}-C=C$$

iso-propyl
(1 H-C)



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2$$ t-butyl (No H-C)

→ It is important to note that although hyperConjugation like inductive effects causes the release of electron & thus the two effects reinForce each other in this respect, the magnitude of the two effects changes in opposite directio in passing along a series of alkyl groups.

$-CH_3$, CH_3-CH_2- , $(CH_3)_2CH-$, $(CH_3)_3C-$

$\longrightarrow$

increase Inductive effect

Decreasing H-C

→ The phenomenon of hyperconjugation can also be applied to group $Cl-CH_2-CH=CH_2$, where the effect operates in the reverse direction

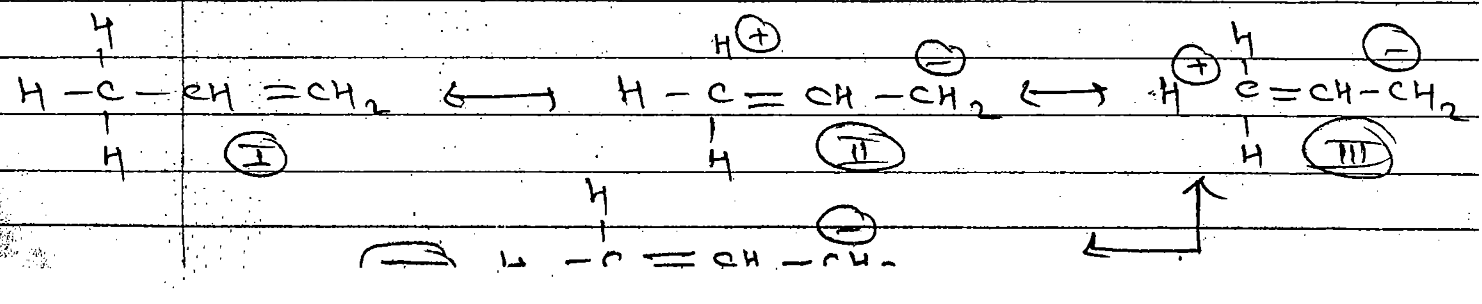
$$Cl-CH_2-CH=CH_2 \longleftrightarrow Cl^{\ominus} \; CH_2=CH-\overset{\oplus}{C}H_2$$

★ Effects of hyperconjugation :

1) Stability of alkenes : H.C explains the stability of certain olefins over other alkenes.

eg.

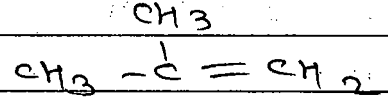
a Propylene is more stable than ethylene because in propylene there are three H-C hyperconjugated bonds & thus the 6 $e^{\ominus}$ of C-H bond can delocalise over three different structures



$$H-\overset{H}{\underset{H}{C}}-CH=CH_2 \; (I) \longleftrightarrow \overset{\oplus}{H} \; H-\underset{H}{C}=CH-\overset{\ominus}{C}H_2 \; (II) \longleftrightarrow \overset{\oplus}{H} \; \overset{H}{\underset{H}{C}}=CH-\overset{\ominus}{C}H_2 \; (III)$$

- In the resonating structures II, III & IV there is no definite bond between one of the carbon atoms & one of the H-atoms, henc hyperconjugation is also known as no-bond resonance.

- Further greater the no. of alkyl groups attache to the doubly-bonded carbons, the more stable the alkene is, thus 2-methyl propene & butene-2- are more stable than propylene



$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$

$CH_3-CH=CH-CH_3$

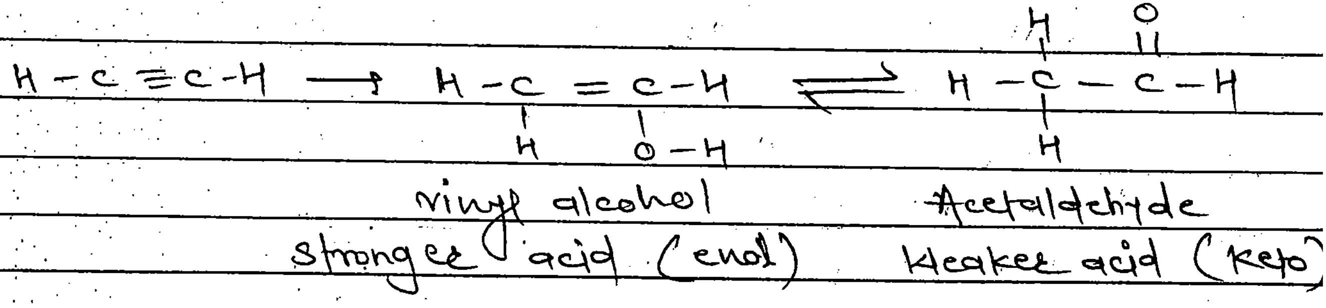
2-methyl propene
(6 H.C)

2-Butene
(6 H.C)

Tautomerism :

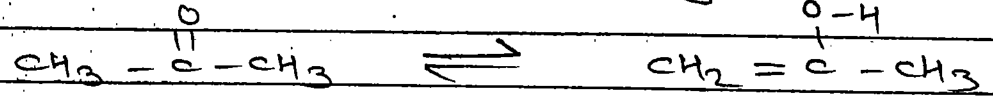
Keto - enol tautomerism :

An example of this phenomenon is found in the hydration of acetylene, the initially formed vinyl alcohol spontaneously rearranges to the isomeric carbonyl compounds. However the equilibrium greatly favours the keto structure.



$$H-C\equiv C-H \longrightarrow \underset{H}{\underset{|}{H-C}}=\underset{O-H}{\underset{|}{C}}-H \rightleftharpoons H-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-H$$

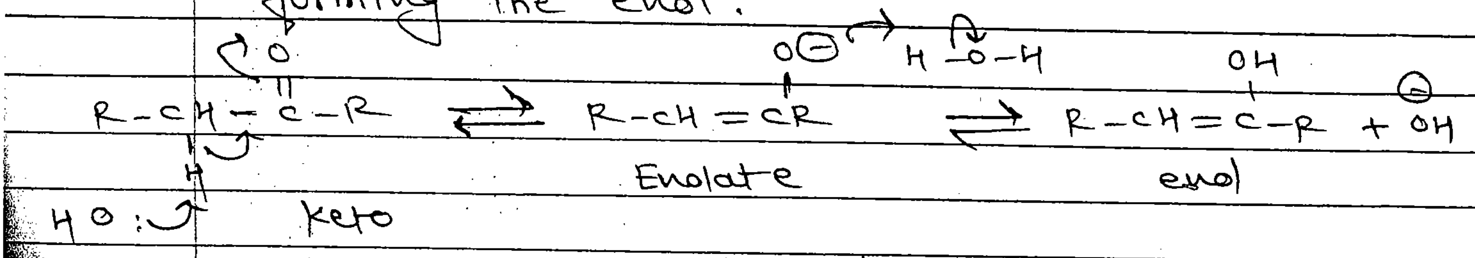
- As is the case with an aqueous solution of acetone the interconversion of keto & enol forms is catalysed both by acids & bases.
- In a basic solution, the base eg. hydroxide ion removes a proton from the α-carbon & the electron are delocalized onto oxygen, to give an enolate.
- Its protonation by water gives the enol



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

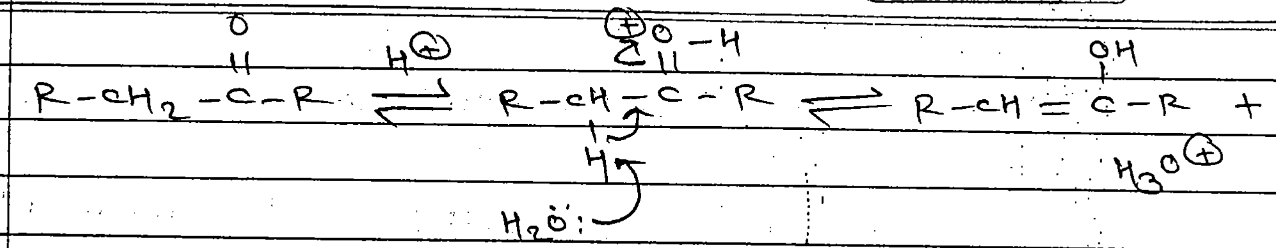
aq. sol^n of Acetone

- In acidic solution, the carbonyl oxygen is protonated & water removes a proton from the α-carbon forming the enol.



$$R-CH_{(H)}-\overset{O}{\overset{\|}{C}}-R \rightleftharpoons R-CH=\overset{O^{\ominus}}{\overset{|}{C}}R \rightleftharpoons R-CH=\overset{OH}{\overset{|}{C}}-R + \overset{\ominus}{O}H$$

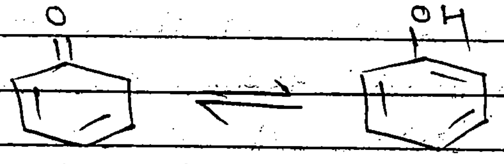
Basic solution.



$$R-CH_2-\overset{O}{\overset{\|}{C}}-R \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R-CH-\overset{\overset{\oplus}{O}-H}{\overset{\|}{C}}-R \rightleftharpoons R-CH=\overset{OH}{\overset{|}{C}}-R + H_3O^{\oplus}$$

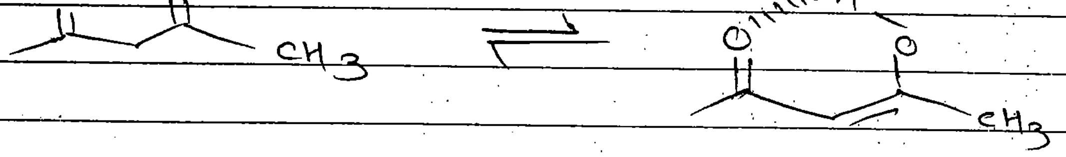
Acidic Solution

- The steps are reversed in the base & acid catalysed mechanism.
- In the base catalysed mechanism, the first step is removal of an α-H & the Second step is protonation of the oxygen.
- In the acid-catalysed mechanism, the first is protonation of the oxygen & the second step is removal of an α-hydrogen.
- Phenol is an usual comp. is that its enol tautomer is more Stable than its keto tautomer that is because the enol tautomer is aromatic but the keto tautomer is not.



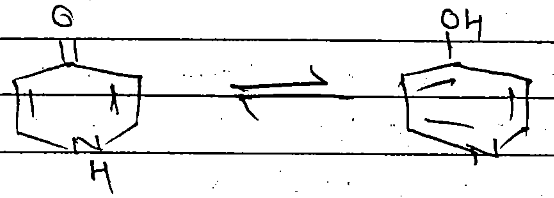
2,4-cyclohexadienone (keto)   phenol (enol)

- In the case of Comp. having a second carbonyl group on the β-carbon i.e. in 1,3-dicarbonyl comp. eg. β-diketone, the fraction of enol tautomer is Considerably more, the enol tautomer in this case is stabilized by hydrogen bonding & also by conjugation of the double bond with the sec. carbonyl group.



Other proton shift tautomerism ;

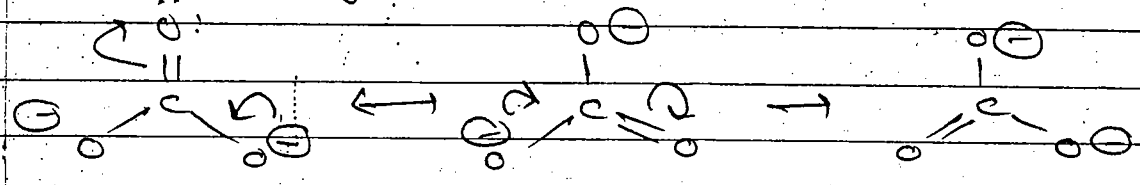
- In several heterocyclic Comp. in the liquid phase or in solution the keto - structure has more stability as in ~~or in sol^n the keto structure has more~~ the case of 4 - pyridone .
- In ethanolic Solution , only the keto Form is detectable while the enolic form predominates in the vapour phase

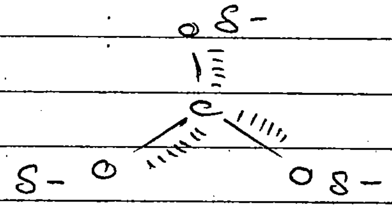


4 - pyridone 4 - hydroxy pyridine .

Resonance ;

- Two or more structures of the same molecule or an ion having identical geometry , possessing the same No. of paired e⊖ but differing in the pairing arrangement of these e⊖ are termed as resonance structures .
- These Structures are shown as related to each other by single double headed arrow (⟷)
- Consider eg. the Carbonate ion (CO_3^{2-})

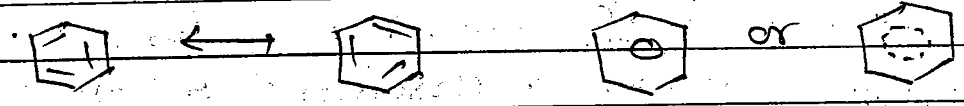




Resonance hybrid

→ Benzene is the classic example to illustrate resonance structures ; Benzene is best described by two equivalent cyclohexatrienic resonance Structure Similarly the three structures of carbonate are equivalent .

→ The importance of resonance Structures becomes apparent in explaining that each c-c bond in benzene is intermediate between a single & double bond as is each c-o bond in CO_3^{2-}



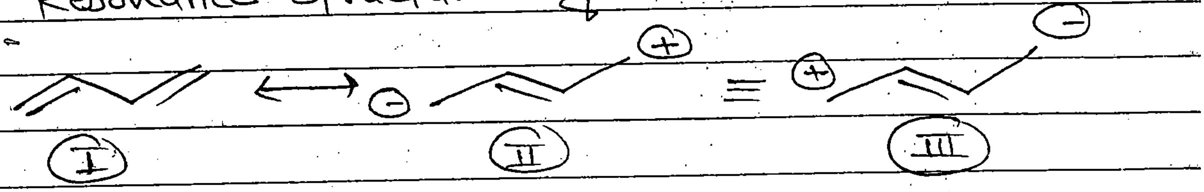
Representation of resonance hybrid of benzene .

→ The problem of writing one best structure to positio the π e⊖ in comp. which may be represented by twc or more equivalent str. is solved by using broken lines Connecting the atoms over which π e⊖ are delocalized .

→ Thus For benzene & carbonate ion the Single resonance hybrid structure showing π e⊖ distributio

→ The resonance structures for the carbonate & the benzene are equivalent . However many molecules car be described by a set as lewis str. that are not equivalent .

eg. Resonance structures of butadiene .



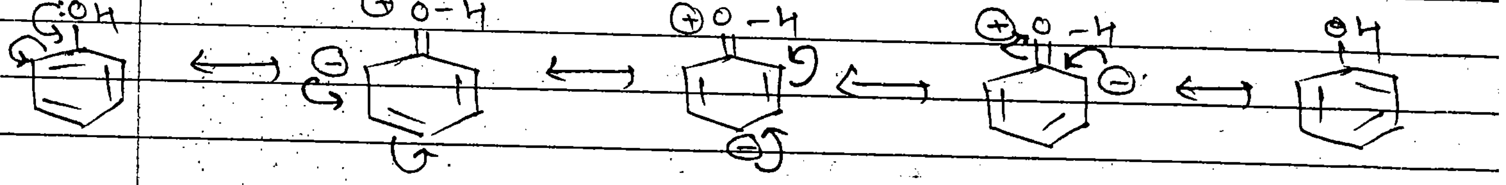
→ The first str. (I) is lower energy than the other two (II & III) which are charge seperated equivale Species .

- Structure (I) make a larger contribution to the ground state structure than either of the charged structures.
- Thus the uncharged str. is the single best representation of butadiene. The fact that, experimentally butadiene shows some double bond character bet- atoms 2 & 3 indicates that charged structures (II & III) also make contribution to the ground state.
- Resonance (Mesomeric) effect is the redistribution of $e^\ominus$ in unsaturated system conjugated with $e^\ominus$, withdrawing or $e^\ominus$ releasing groups.
- The $e^\ominus$ attracting mesomeric effect is indicated by −M effect & the $e^\ominus$ repelling mesomeric effect is indicated by +M effect.

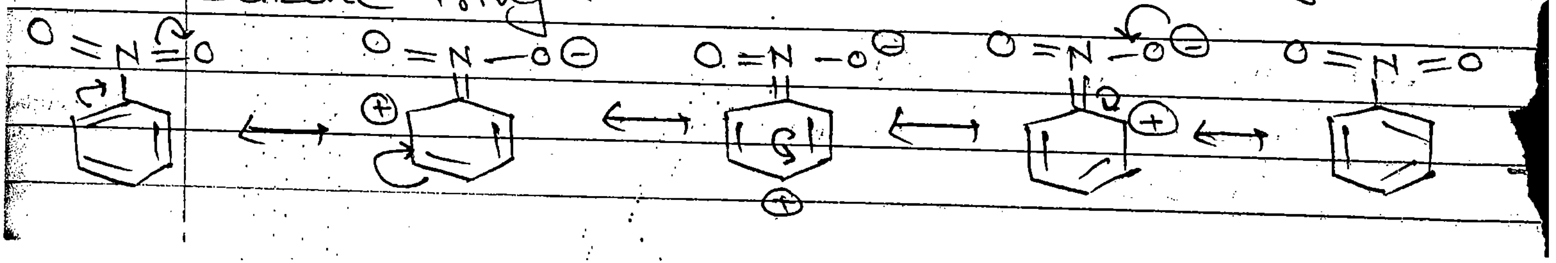
+M effect possessing groups : $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, $-SR$, $-X$ etc.

−M effect possessing groups : $-CHO$, $>C=O$, $-CN$, $-NO_2$, $-SO_3H$ etc

- The acidity of phenol is due to +M effect of OH groups. The mesomeric transfer of the loan pair on the oxygen atom of the phenol to the π $e^\ominus$ of the benzene ring results in several resonance str.



- Nitrobenzene shows −M effect by withdrawing $e^\ominus$ from benzene ring.



Aromaticity :

→ The aromatic Compounds generally Contains alternate double & single bonds in a cyclic structure & resemble With benzene in chemical behaviour.

→ Rules for Aromaticity :

To know Whether a particular Comp. is aromatic or ~~anti~~ non-aromatic.

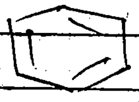
① An aromatic Comp. is Cyclic & planar, unhybridised

② Each atom in an aromatic ring has a P-orbital. These P-orbitals must be parallel So that a Contineous overlap is possible around the ring.

③ It must have cyclic cloud of delocalised $\pi\ e^{\ominus}$ above & below the plane of the molecule must be cyclic having Conjugated π-bonds.

④ The π - molecular orbital ($e^{\ominus}$ cloud) Formed by overlap of P-orbitals must Contain $(4n+2)\ \pi\ e^{\ominus}$ Known as Huckel rule.

Examples :



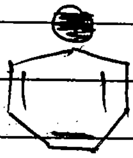
$6\pi e^{\ominus}$

Benzene

- Cyclic, planar, 3 alternative double bonds of the ring has sp^2 orbitals ($e^{\ominus}$) hence according to Huckel rule.

$$4n + 2 = \pi\ e^{\ominus}$$
$$4\times1 + 2 = 6\ \pi e^{\ominus}$$

obeys the Huckel rule.



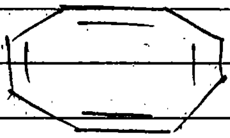
Cycloheptatriene

- Cyclic, planar, 3 db & $6\ \pi\ e^{\ominus}$ but one carbon is sp^3 hybridised, so there is no P-orbital. Hence no Contineous cyclic cloud of $e^{\ominus}$ even though this Comp. obeys Huckel rule.

- Not aromatic.

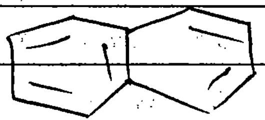
Page :
Date : /

Cyclooctatetraene :

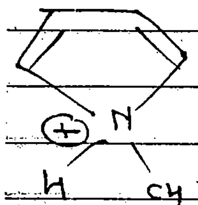


- cyclic, planar, 4 db & $8\pi e^{\ominus}$
Does not follow Huckel rule.
$4\times n + 2 = 8\pi e^{\ominus}$
$4n = 8-2$
$4n = 6 \quad n = 6/4 = 1.5$

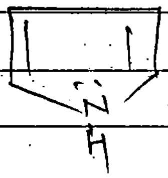
So n is not integer so, it is not aromatic.

Napthalene :  $10\pi e^{\ominus}$

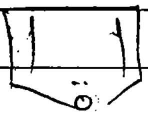
$4n+2 = 10\pi e^{\ominus}$
$4n = 10-2$
$\therefore 4n = 8 \quad n = 8/4 = \underline{2}$



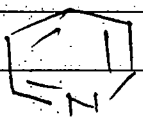
Aromatic
Anti-Aromatic



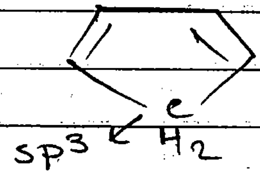
$6\pi e^{\ominus}$
$4n+2 = 6\pi e^{\ominus}$
$4n = 4\pi e^{\ominus}$
$n = 1$



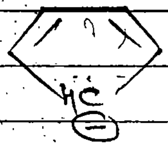
$6\pi e^{\ominus}$
Aromatic



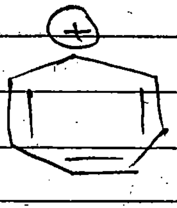
$6\pi e^{\ominus}$
Aromatic



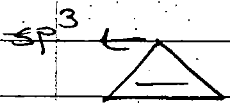
Cyclopentadiene
$4\pi e^{\ominus}$
not aromatic
~~(Anti aromatic~~)



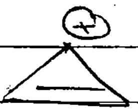
$6\pi e^{\ominus}$
Aromatic



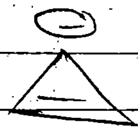
Tropylium cation
$6\pi e^{\ominus}$
Aromatic.



$2\pi e^{\ominus}$
Not aromatic

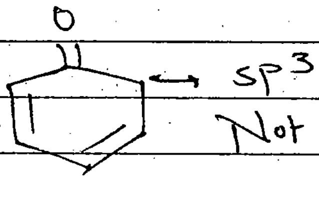


$2\pi e^{\ominus}$
Aromatic.



$4\pi e^{\ominus}$ Anti Aromatic.

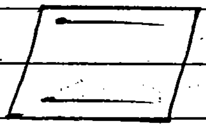
Aromatic



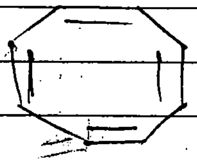
Not - aromatic

Antiaromaticity :

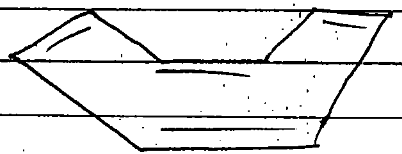
- All atoms must be sp^2 or sp hybridised.
- Planar Conjugated System less stable than corrospon ding a cyclic unsaturated species are called Antiaromatic.
- Molecular ~~ob~~ orbital Calculations have shown tha such Compounds have $4n\ \pi\ e^{\ominus}$ are called such cyclic Comp. Which have $4n\ \pi\ e^{\ominus}$ are antiaromati Comp. & this property is called antiaromaticity ~~Comp~~.
- Antiaromatic Compounds are cyclic planar & possesses fully delocalised $4n\pi$ electrons.

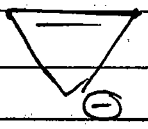


Cyclobutadiene
$4\ \pi\ e^{\ominus}$



Cyclooctatetraie
$8\ \pi\ e^{\ominus}$
it is not planar
but tub-shaped
|||



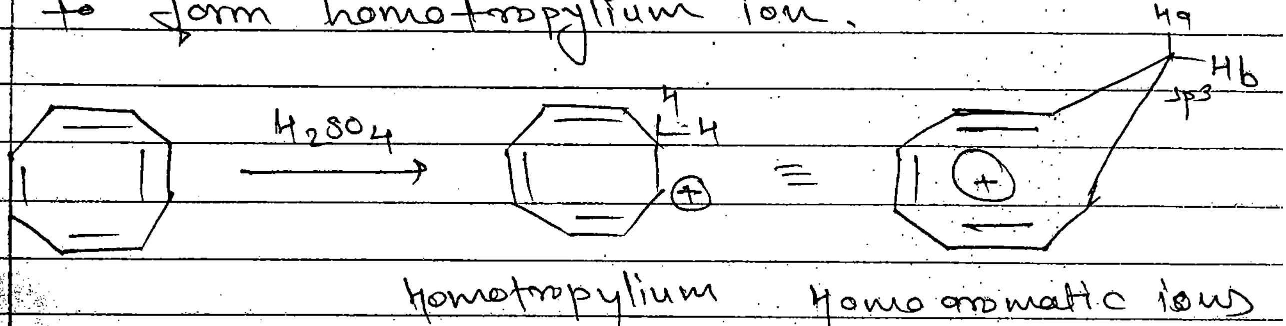


$4\pi\ e^{\ominus}$
Antiaromatic.

Homo Aromaticity :

neither Ar & nor Anti Ar

- The Compounds or ions that Contains one or more sp^3 hybridised carbon atoms in an Conjugated ring is called as Homoaromatic Compound.
- When cyclooctatetraene is dissolved in conc. H_2SO_4, a proton adds to one of the db to form homotropylium ion.



Homotropylium cation.

Homo aromatic ions Cations.

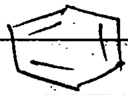
sp^3 hybridised carbon atoms are force to lie almost vertically above the plane of Ar. system.

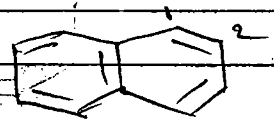
Aromaticity in benzenoid & non-benzenoid Comp.

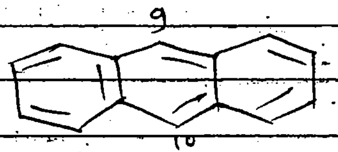
- Aromatic Compounds may be benzenoid or non-benzenoid
- Benzenoid Compounds have at least one benzene ring in the molecule which shows complete delocalisation in the ring. Whereas the non-benzenoid Compounds do not have any benzene nucleus but shows proper Conjugation and follows Huckel rule

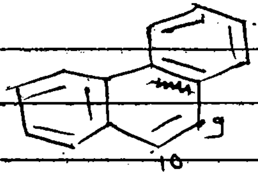
Benzenoid :

Examples : Benzene, Napthalene, phenanthrene & anthracene.









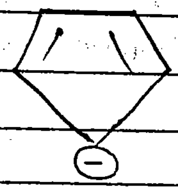
Benzene	Napthalene	Anthracene	phenanthrene
6 π e⊖	10 π e⊖	14 π e⊖	14 π e⊖
Aromatic	Ar.	Ar.	Ar

→ out of phenanthrene & Anthracene, phenanthrene is more stable because anthracene can write only four resonance structure but phenanthrene have five resonating structures.

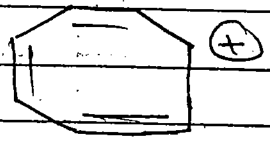
→ In Napthalene 1,2 position is active while in Anthracene & phenanthrene 9, 10 position is active for substitution reaction.

② Non benzenoid Aromatic Comp :

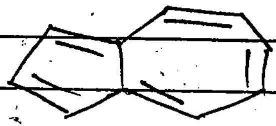
Examples : cyclopentadienyl anion , cycloheptatrienyl cation & some aromatic annulene

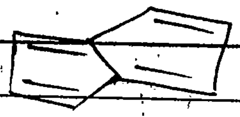

Aromatic
obeys Huckel
rule .

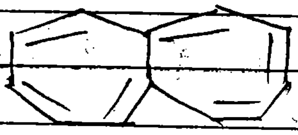
cyclopentadienyl
anion


Aromatic

cycloheptatrienyl
cation


Azulene
10 π e⊖ (Aromatic)

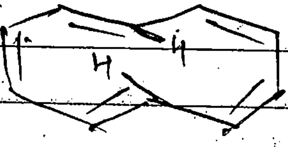

Pentalene
8 π e⊖
Antiaromatic


Heptalene
12 π e⊖ (Antiaromatic)

- Azulene is regarded as a Combination of Cyclopentadienyl anion & Cycloheptatrienyl cation (tropylium ion).

Hence Concluded that if a bicyclic System having 10 e⊖ it spread over two rings are aromatic

- If we Consider Cyclodecapentaene it also contains 10 e⊖ but it is non-aromatic since hydrogen atom Created steric hinderance .

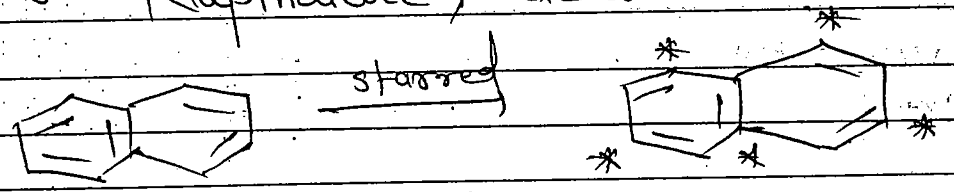

Cyclodecapentaene / [10 Annulene
Non - aromatic .

★ Alternate & Non-alternate Hydrocarbons

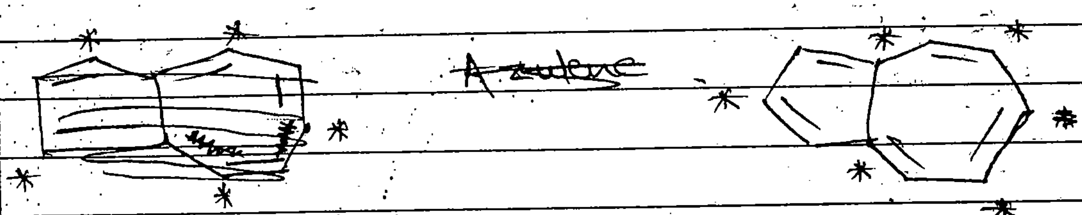
- No two atoms of the same set are not directly linked called as alternate hydrocarbon.
- Two atoms of the same set are directly linked called as Non-alternate hydrocarbon.

eg. Napthalene, azulene

starred


(Alternate)

~~Azulene~~


Azulene (Non-alternate)

Even Alternate hydrocarbons :

They contain even no. of conjugated atoms, i.e. an equal no. of starred & unstarred conjugated atoms,

eg. 1,3-butadiene.

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

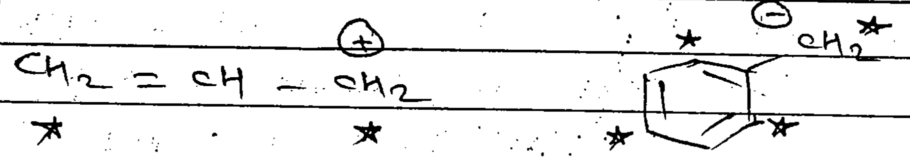
1,3,5 - hexatriene

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

- Aliphatic & aromatic even ~~Eo~~ hydrocarbons contain only two types of molecular orbitals, bonding & antibonding.
- No. of bonding molecular orbitals & non-bonding are always equal in alternate hydrocarbons.
- In alternate hydrocarbons all the bonding molecular orbitals are filled & the pi-electrons are uniformly spread over the unsaturated atoms.

II Odd - alternate hydrocarbons.

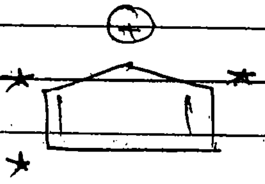
- Hydrocarbons Contain odd no. of Conjugated atom
- ~~odd~~ alternate hydrocarbons are generally carbocation carbanion or Free radical.
- In odd alternate hydrocarbons no. of starred & unstarred atoms are not same

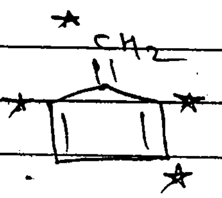

$\overset{*}{C}H_2 = CH - \overset{\oplus}{\overset{*}{C}H_2}$

- Contain three types of molecular orbitals, bonding non-bonding & Antibonding orbitals
- Bonding orbitals always equals to ~~ve~~ Anti-bonding orbitals.

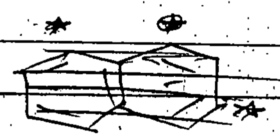
Non - alternate hydrocarbons :-

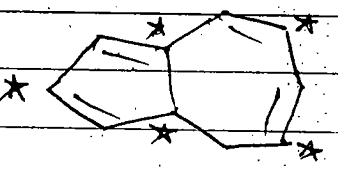
- The energies of bonding & ~~no~~ anti-bonding orbitals are not equal & apposite & charge distribution are not the same in cation, anion & radical.
- The Conjugated atoms may be even & odd, may be divided into two sets such that two atoms of Some set is linked to each other.





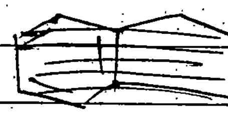
Fulvene

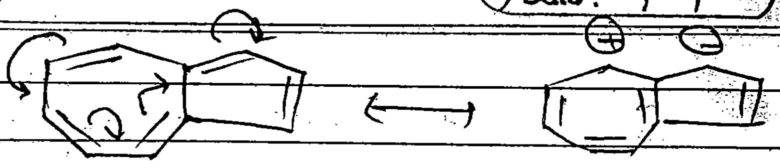




Azulene.

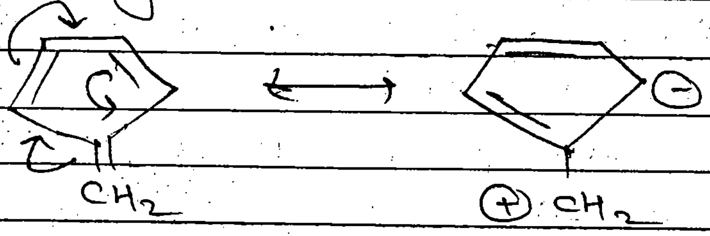
- In azulene, electrophilic substitution reac^n occurs in five membered ring due to delocalization of $e^{\ominus}$.
- Azulene is slightly dipolar & in 5 membered ring there is more $e^{\ominus}$ density as Compared to 7 membered ring.



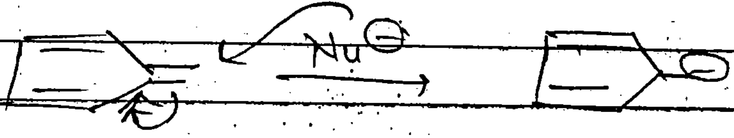


Fulvene :

→ Cyclic & planar, all sp^2 orbitals, $6\pi e^{\ominus}$ obeys Huckel's rule but still non-aromatic because all $6\pi e^{\ominus}$ do not reside within the ring ~~results in the terminal carbon~~ moving the $C=CH_2$ $\pi e^{\ominus}$ into the ring results in the termina carbon being electron deficient.

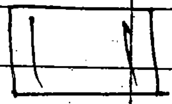


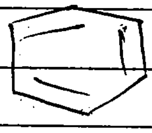
When $Nu^{\ominus}$ attacks the exocyclic carbon atom of the non-aromatic Comp, the $e^{\ominus}$ from the $C=C$ π bond go to the endo cyclic carbon & makes the ring aromatic.

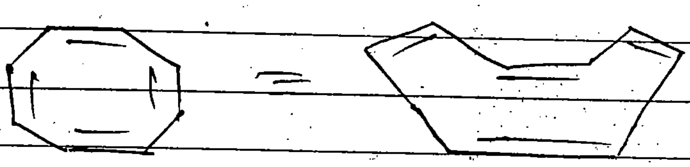


★ Annulenes :

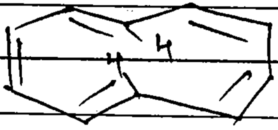
- Annulene is a general name for monocyclic hydrocarbons with alternating single & double bonds
- The ring size of annulene is indicated by a no. in brackets.
- Annulene must have an even no. of carbon atoms, the aromaticity of cyclobutadiene a [4] Annulene, Benzene is [6] Annulene & Cyclooctatetraene [8] Annulene.







[4] Annulene	[6]	[8]
cyclic, planar	cyclic, planar ~~pl~~.	cyclic but not planar
$4n\pi$ $e^{\ominus}$	$4n+2\pi$ $e^{\ominus}$	$4n\pi$ $e^{\ominus}$
Antiaromatic.	Aromatic.	Not-aromatic

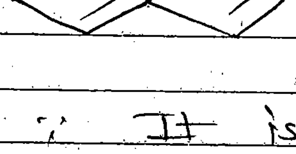


→ [10] Annulene : Cyclodecapentaen

This comp. contains trans db but due to interference of H at C_1 & C_6 it can not attain co-planarity (Non-planar) hence does not exhibit aromaticity

(unstable)

→ But the stable derivatives of [10] Annulene where ($X - CH_2$, O, NH_2) in which the interfering H is replaced by a methylene bridge the 10 membered ring becomes flatten to permit π $e^{\ominus}$ delocalisation & develops aromatic stability by Huckel's rule.

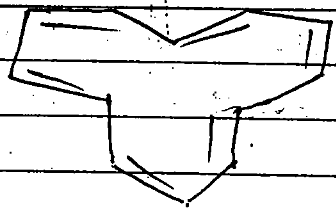


1,6 - methano [10] Annulene

Replacing H with methylene bridge removes the transannular interactio

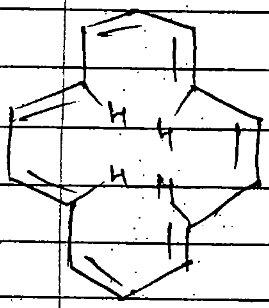
∴ It is Aromatic.

- [12] Annulene :



12 πe⊖
possess 4nπ e⊖
Hence Anti-aromatic.

- [14] Annulene :

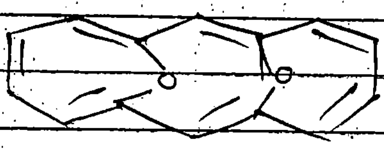


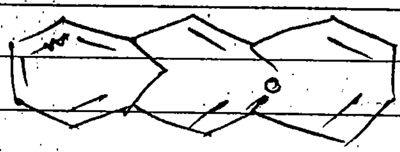
Follows Huckel rule (4n + 2) πe⊖
Overlapping of -H, disturbs the planarity of molecule.
- All C-C bonds are of equal length but molecule is not planar.

[14] Annulene is aromatic though it is not planar. but the overlapping ~~of~~ of H reduces its aromaticity. ∴ It is not very stable.

Variety of [14] Annulene are prepared with both Carbon & heteroatom bridges.

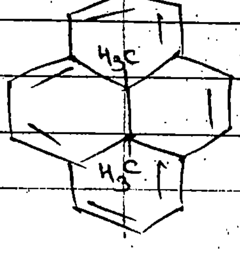
eg.
Syn 1,6 : 8,13 - Bisoxio [14] Annulene





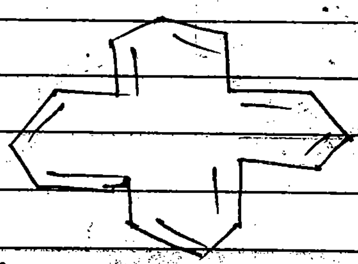
Syn 1,6 : 8,13 - Oxiodo methano [14] Annulene

obey's Huckel rule Hence Aromatic.

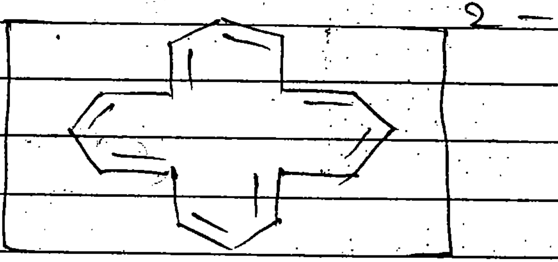


Trans dimethyl dihydropyrene : Absence of non-bonded interactions of hydrogens. It is more stable than [14] A

[16] Annulene :



[16] Annulene
Antiaromatic



18 π $e^{\ominus}$ Aromatic

Both [12] & [16] Annulene are not planar They have flexibility to adopt non-planar Conformations

∴ Both of these do not show Antiaromaticity

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Unit I :- Aromaticity

Aromaticity :

The aromatic compounds generally contains alternate double & single bonds in a cyclic structure & resemble benzene in chemical behaviour. They undergo substitution rather than addition reactions. This characteristic behaviour is called Aromatic character or Aromaticity.

Aromaticity is in fact a property of the sp^2 hybridized planar rings in which the p-orbitals allow cyclic delocalisation of π-electrons.

Some aromatic properties are given

1) Unusual stability :

They have low heat of hydrogenation & low heat of combustion. Heat of hydrogenation of benzene is $\boxed{-49.8}$ kcal/mole where as cycloheptatriene is 85.5 kcal/mole. Simillar heat of combusion of benzene 789.7 is low as compaired with cycloheptatriene about 824.1 Kcal/mole.

2) Substitution rather than addition :-

Eventhough aromatic compound contain double bonds, they do not take part in ~~addim~~ addition reaction but they undergo electrophilic substitution like nitration, halogenation, sulphonation & friedal craft reaction etc.

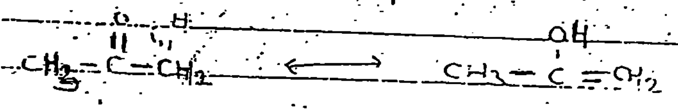
3) Aromatic compounds are not easily oxidised by aq. $KMnO_4$, HNO_3 etc.

4) Cyclic flat molecule :

Aromatic compd generally contain 5, 6 or 7 membered ring & they are having flat ring

The keto form differs from the enol as it posses C-H. a C-C & a C=O bond where the enol has a C=C a C-O & O-H bond. The sum of the three bonds of keto form is 355 kcal/mole while sum of bonds of enol form is 347 kcal/mole hence the keto form is stable than enol form.

e.g. Acetone exhibits tautomerism. It is a equilibrium mix. of two isomers.



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longleftrightarrow CH_3-\overset{OH}{\overset{|}{C}}=CH_2$

keto enol

keto form changes into enol form by migration of proton to carbonyl oxygen then a pair of electron shift from the C-H bond to C-C bond.

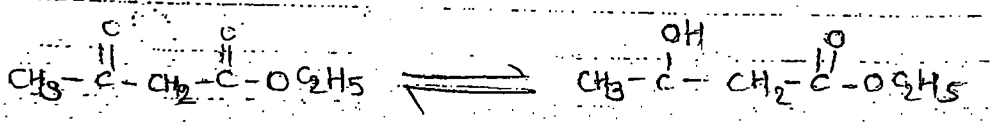
Difference betⁿ tautomerism & Resonance :

① The tautomers are distinct molecules while resonance forms have no clear independent existence.

② In tautomers both electrons & atoms will change position but in resonance only electron will change the position.

③ In tautomerism proton H: migrates from a carbon to carbonyl oxygen.

e.g. Acetoacetic ester



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$

keto-form enol-form

Aromatic
nonaro—
antiaromatic — 4n πe
not benzene & [illegible] sp^2 — aromatic
n=0

Rules For Aromaticity :-

On the basis of above properties there are some rules which helps us in knowing whether a particular compound in aromatic or non aromatic.

1) An aromatic compound is cyclic & planar.

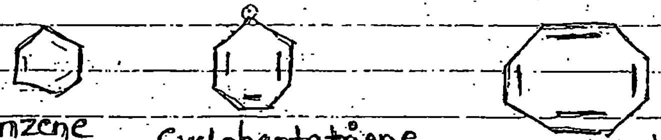
2) Each atom in an aromatic ring has a p orbital. These p-orbitals must be parallel so that a continuous overlap is possible around the ring.

3) It must have cyclic cloud of delocalised π-electron above & below the plane of the molecule must be cyclic having conjugated π-bonds.

4) ~~The π molecular orbital (electron cloud)~~ formed by overlap of p-orbitals must contain $(4n+2)$ pi electrons.
where n is integer 0, 1, 2, 3, 4 etc
This is known as Huckel rule.

Thus according to Huckel rule the no. of π e⁻ is an aromatic comp. may be 2 (n=0) 6 (n=1), 10 (n=2), 14 (n=3), 18 (n=4) etc

Let us apply these rules to the following examples



Benzene   Cycloheptatriene   Cyclo~~[illegible]~~tetraene

① Benzene :-

i) It is cyclic planar compound having three alternative double bonds thus each carbon of the ring has sp^2 orbitals (electrons) hence according to Huckel rule

$4n+2 = \pi e^{\ominus}$

$4n+2 = 6 \quad 4n = 6-2 \quad \therefore n = 1$

since n=1 it is an integer so benzene obeys Huckels rule so it is aromatic.

② Cycloheptatriene

It is cyclic & planar. It has three double bonds & 6π electrons.

But in this case one of the carbon is saturated (sp3) hybrid & so there is no p-orbital.

Hence there is no continuous cyclic cloud of πe even though this compound obeys Huckel rule.

It is not aromatic since there is no continuous cloud of $\pi e^{\ominus}$

③ Cyclooctatetraene :

This is having four alternative double bonds so no of π electrons are eight. This does not come under Huckel rule

$4n+2 = 8$

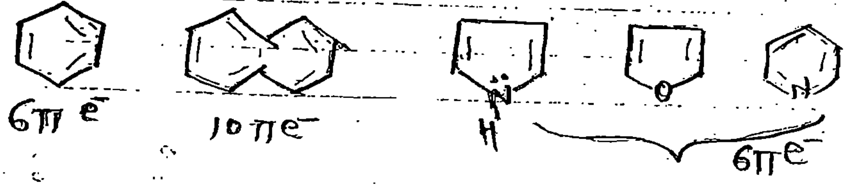
$4n = 8-2$

$4n = 6 \quad n = \frac{6}{4} = 1.5$

so n is not an integer so it is non-aromatic

Hence aromatic compounds may be benzenoid (having benzene nucleus) or nonbenzenoid (without benzene ring) all that is required for aromaticity with $(4n+2)\pi e^{\ominus}$ i.e as a continuous πe cloud above & below plane of ring with high resonance energy

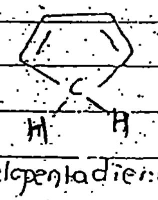
following cyclic comp are having all the above properties hence these are aromatic.

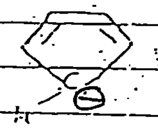


In addition to the above neutral molecule there are no. of cyclic ions which are ~~no. of~~ aromatic according to Huckel rule.

Five membered Carbocyclic Compounds :-

i) Cyclopentadiene is not an aromatic compound since its energy is very low 3 kcal/mole. But cyclopentadienyl anion having aromatic character.

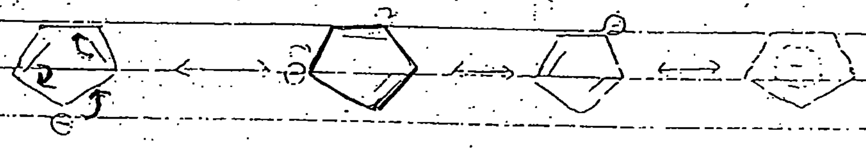

cyclopentadiene


Cyclopentadienyl anion

i) ~~This anion is having six π e⁻~~ - Four π e⁻ of two double bonds & one of the methylene carbon atom & one of the H-atom.

ii) Hence it is having $(4n+2)\pi e^-$. According to Huckel rule it is having aromatic character.

iii) The negative charge on the anion is delocalised among the carbon atom. This ring is having 42 kcal/mole resonance energy.

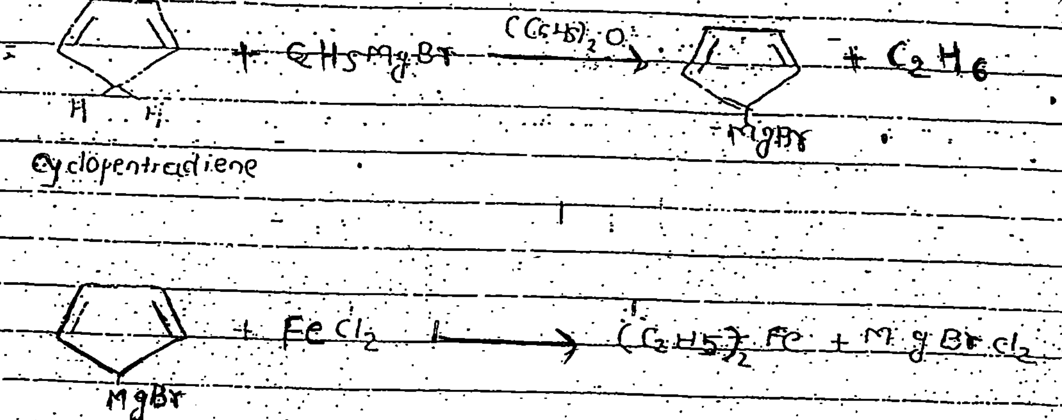

(canonical structure of cyclopentadienyl anion)

iv) The aromatic character of cyclopentadienyl anion is conformed by the isolation stability of its Eui

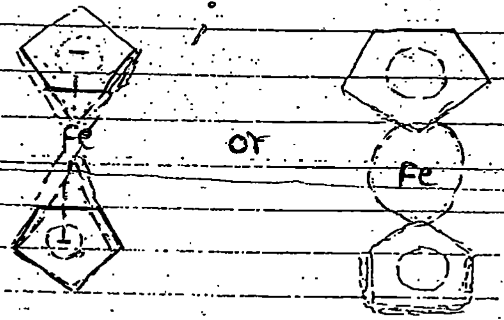
e.g. Ferrocene [Dicyclo pentadienyl iron]

This is most imp example of non-benzonoid compound

Preparation of Dicyclopentadienyl iron :



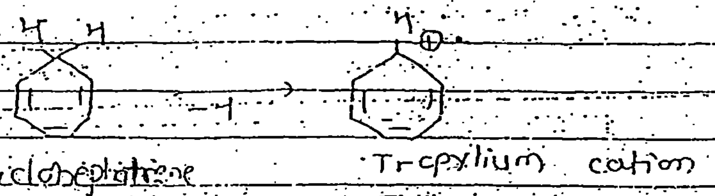
In the formation of this compound partial reduction on Ferrous salt involved Hence it was known as Ferrocene



Ferrocene is an orange solid. It's structure was found by x crystallography In its structure ferrous ion is present betn five parallel & equidistance cyclopentadienyl ion placed about 3.4 A°

Seven Membered ring :

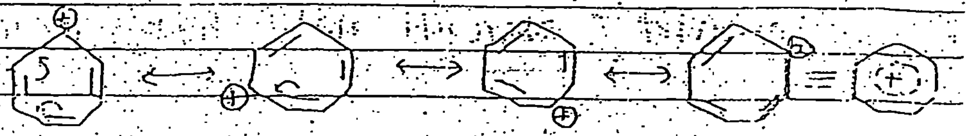
The seven membered unsaturated hydrocarbon like cycloheptatriene behaves as a triene indicated by its low resonance energy But removal of one hydrogen ion gives carbonium ion i.e tropylium cation



Tropylium cation possesses aromatic behaviour due to following reasons-

i) It has planor ring.

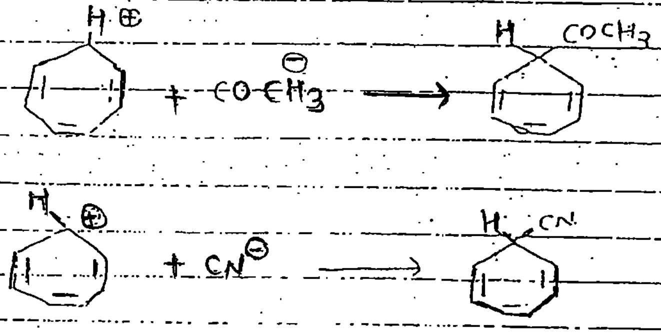
ii) Effective delocalisation of a -ve charge takes place as-



Tropylium ion has six $\pi e^{\ominus}$ ($2e^-$ of 3 double bonds) so it is aromatic on the basis of Huckels rule $(4n+2)\pi e^-$

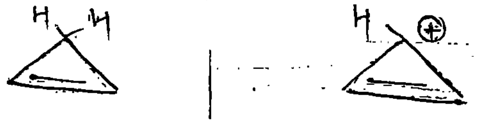
PMR Spectra of tropylium ion shows only one signal indicates that all protons are identical

Tropylium Cation also undergoes SN reaction



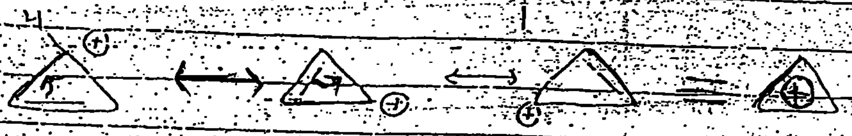
Three Membered ring :-

cyclopropene is non-aromatic in nature but cyclopropylene ion is aromatic in nature



~~In addition to~~

In the cyclopropylene cation distribution of charge takes place as follows



It obeys Huckels rule i.e. $4n+2=2$ where $n=0$ It is having aromatic according huckel rule

Imp

Alternate & Non-Alternate Hydrocarbons

Conjugated hydrocarbons may be devided into two types alternate & non-alternate

1) Alternate Hydrocarbons :-

In the alternate type the atoms can be devided into two sets one starred & the other unstarred in such a way that no two atoms of the same set are directly linked

e.g. Benzene & Napthalene are alternate hydrocarbon.

no of starred = no of unstarred

The even alternate hydrocarbons are those with equal number of starred & unstarred atoms having equal number of bonding & antibonding π molecular orbitals. The bonding orbitals are filled in the ground state

even
2 star = 2 unstarred

odd
5 & 4
2 & 3

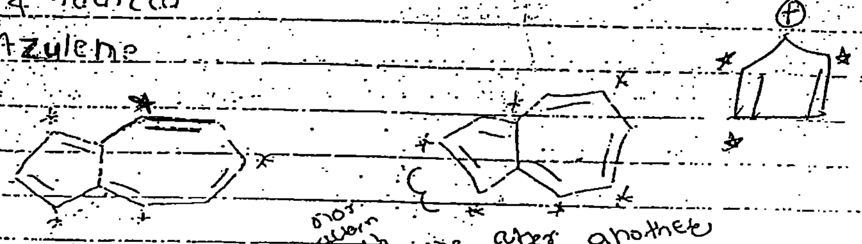
The odd alternate hydrocarbons are those having odd number of conjugated atoms must occur as radicals, carbonium ions or carbanions They have a non-bonding π-molecular orbitals of zero bonding energy when an odd no. of orbitals overlap. an odd no. is created e.g. In Benzylic system the cation has unoccupied non-bonding orbital, the free radical has one electron with there & the carbanion two.

Moreover benzene & napthalene containing even no. of C-atoms are called as even & are all alternate hydrocarbon while allylic cation radical, anions containing odd number of C-atoms called odd alternate hydrocarbons

Non-Alternant Hydrocarbons :

In nonalternate hydrocarbons the energies of bonding & antibonding orbital are not equal & opposite. And charge distribution are not the same in **cation** anion & radical

e.g. Azulene

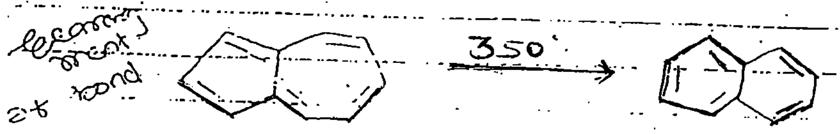


Azulene : bicyclic nonbenzenoid aromatic compound.

Azulene is a deep blue compound. It is most studied polycyclic non benzenoid hydrocarbons

It is isomer with napthalene but it is less than napthalene.

When azulene is heated - above 350° in absence of **air** it is converted quantitatively into napthalene



Azulene can be written as fused cyclopentadiene & cyclo heptatriene ring.

Individually they are not Aromatic but in dipolar structure azulene satisfies the Hückel rule $(4n+2)\pi e^{\ominus}$ Here $n=2$ Hence it shows aromaticity.

The important aromatic character exhibited by azulene are given below.

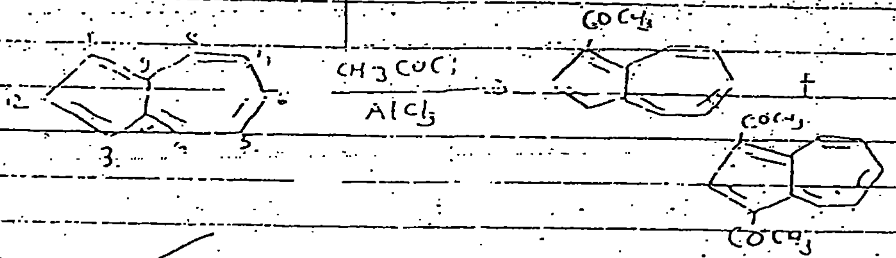
1) Azulene do not undergo oxidation & do not polymerises.

2) Like napthalene azulene form molecular compound with picric acid.

3) Azulene does not behave as diene. It does not undergo Diel's Alder reaction with maleic anhydride.

Azulene undergo substitution electrophilic reaction e.g. Nitration, halogenation, Friedel craft reaction & coupling reaction with diazonium salt.

~~The electrophilic substitution takes~~ place in position 1 & 3 according to dipolar structure.

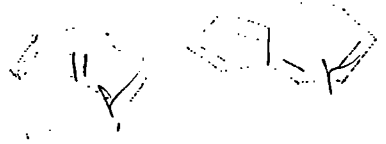


Annulenes :

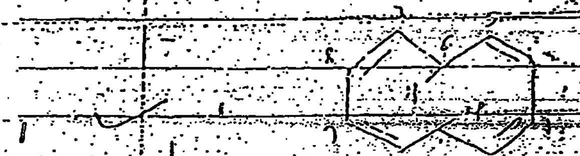
conjugated Monocyclic polyenes (C_nH_n) hydrocarbon containing 10 or more C-atoms in a ring are called Annulenes.

Annulenes are named as (n) Annulene where n is the no of carbon atoms.

e.g (10) annulene (cyclo decapentacene) is the simplest annulene having strain less planar ring. It is very unstable apparently because of the nonbonded interaction.



of the hydrogens inside the polar ring

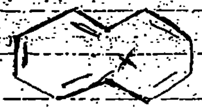


Trans double bonds

(10 Annulene cyclodecapentaene)

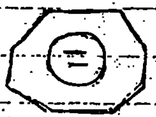
This comp. contains trans double bonds but due to interface betn interference 1 & 6 H-atom, ~~it~~ can not attain coplanarity (Non planar) & hence does not exhibit aromaticity.

But the stable derivatives of to annulene where (X = CH_2, O, NH) in which the interfering H is replaced by a methylene bridge the 10 membered ring becomes flatteren to permit π e⁻ delocalisation & develops aromatic stability by Huckel's rule.

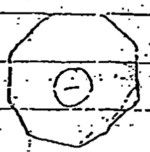


X = CH_2, O, NH

cyclooctatrienyl dianion & ~~cyclooctatrien~~ cyclononatetraen anion have been prepared as the potassium & the lithium salt resp.

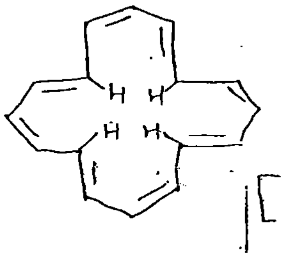


cyclooctatrienyl dianion



cyclononatetraenyl anion

one of the most interesting examples is the trans-dimethyl dihydropyrene shows aromatic stability of much higher than 14-annulene



[14] Annulene

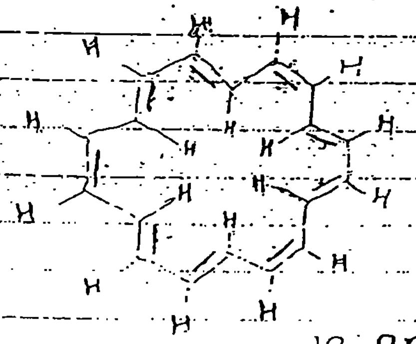
14-Annulene

trans dimethyl
dihydropyrene

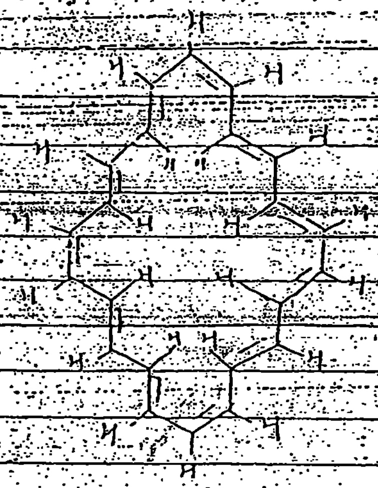
This is explained in trans-dimethyl dihydropyrene, the absence of nonbonded interactions of the hydrogens inside the planar ring. It also undergoes bromination, nitration & Friedel crafts reaction under mild conditions.

18 Annulene & 22 annulene are aromatic because of if we go by their NMR spectra. The π-electrons in aromatic compounds due to the induced ring it produces shielding effect on the inner protons & deshielding effects on the outer protons & ~~desh~~ These annulene shows simillar NMR characteristics.

Thus Huckel's rule also fails to explain the aromaticity even in $(4n+2)$ $(4n+2)\pi e^-$ systems in 18 & 22 annulene. It must be noted that $(4n+2)$ annulenes which are not aromatic still remains relatively more stable than their neighbouring 4n annulenes.



18 annulene

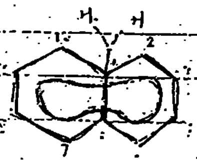


22-Annulene

Medium size annules are aromatic only on the basis of magnetic measurments chemically they show no aromatic stability rather they are very reactive & polymerse radially like polyenes.

The decrease in aromaticity is explained firstly by increasing tendency of π-bonds with increasing ring size to favour alternating structures with localized bonds & secondaiy by the non-bonded interaction among the hydrogens inside the planar rings of the medium size annulenes.

Vogel synthesized 1,6 methanocyclic decapentane. This is pale yellow solid & shows aromaticity.



It undergoes electrophilic substitution reactions as acylation, Halogenation, nitration at 2 & 7 position

The annulenes so prepared are
n = 12, 14, 16, 18, 20, 24 & 30
out of which only [14], [18] & [20]

annulene have $(4n+2)\pi e$ - The other are $4n$ molecules & behave like olefins.

[18] annulene was the 1st comp. prepared It is cyclic planar containing $(4n+2)\pi e$ hence it is aromatic.

Aromaticity decreases in the order benzene > naphthalene > anthracene > tetracene > pentacene > hexacene > heptacene with 6, 10, 14, 18, 22, 26 & 30 carbon atoms. The higher member of this series show extreme reactivity & are very unstable.

Only the Huckel rule does not account for the difference in aromatic stability of the above hydrocarbons & the angularly fused isomeric hydrocarbons which are more stable.

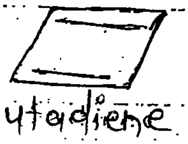
i.e. Huckel's rule is therefore not suitable for predicting aromatic stability in polycyclic hydrocarbons.

Antiaromaticity :

"Planar conjugated system less stable than corresponding a cyclic unsaturated species are called Antiaromatic."

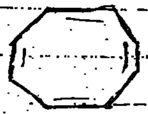
Molecular orbital calculations have shown that such compounds have $4n\pi e$ are called such cyclic comp. which have $4n\pi e$ are called antiaromatic comp. & this property is called antiaromaticity.

Antiaromatic compounds are cyclic planar & passeses fully delocalised $4n$ π electrons.



cyclobutadiene

$4\pi e^{\ominus}$

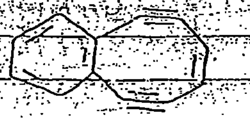


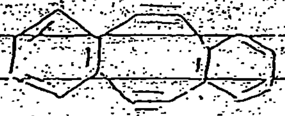
cyclooctatetraene

$8\pi e^{\ominus}$

It has been shown experimentally that conjugated ring 2, 6, 10 & 14 πe are aromatic while those with 4, 8, 12, 16 & 20 are Antiaromatic eg cyclooctatetraene is not plana but tub shaped. Therefore we would except it is neither aromatic nor antiaromatic. Both these conditions require overlap of parallel p orbitals.

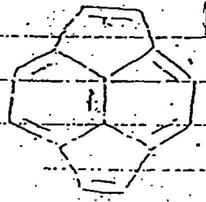
However, cyclooctadienes are planar conjugated eight electron systems (the four extra triple bond electrons do not participate) which NMR shows antiaromaticity.



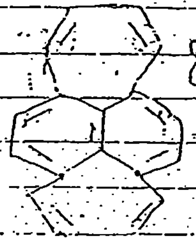


The compounds such as peracyclene & dipleradiene have been expected to behave like napthalenes with outer bridges - but instead the outer π frameworks systems the 12 & 16 electrons constitute antiaromatic system with an extra central double bonds.

pyracylene



Peracycline



Dipleradiene

Therefore we can conclude that in 4nπ systems antiaromaticity would be at a maximum where a molecule is to be planar

Homoaromaticity

When cyclooctatetraene is dissolved in conc. H_2SO_4 a proton adds to one of the double bond to form homotropylium ion. In this species an aromatic sextet is spread over 7 carbons as in tropylium ion. The 8th carbon is sp³ hybridised carbon & so can not take part in the aromaticity.

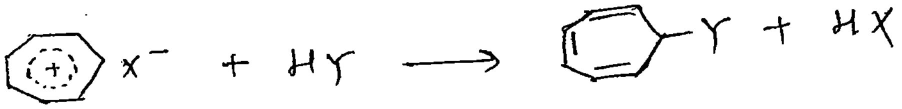
The imp feature of this NMR spectra of this cation is that proton a & b exhibit sharply difference chemical shift. Proton a is showing upfield of b indicating the existence of Aromatic. This is an example of homoaromatic compound which may be defined as compound that contain one or more sp³ hybridised C-atom in a conjugated cycle.

All the homoaromatic compound so far discovered are ions & it is questionable as to wheather homoaromatic character can exist in uncharged system.

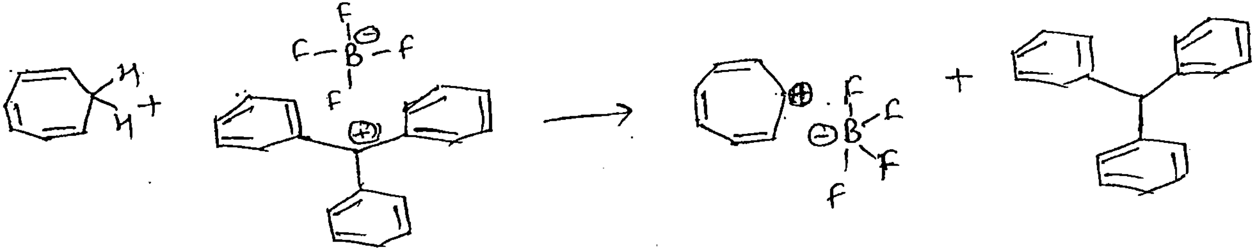
Homoaromatic ions of two & ten electrons are also known.

8

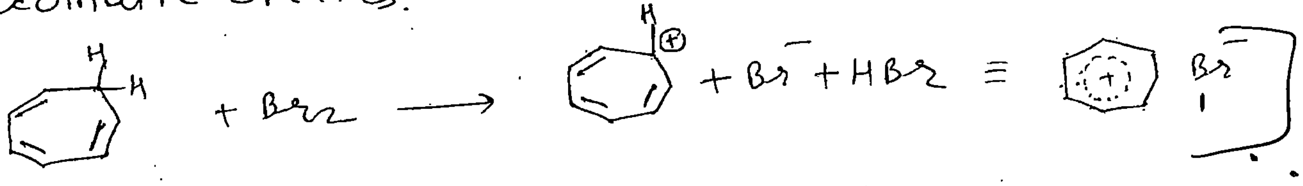
- Nucleophiles including weak acids, convert tropylium salts into substituted cycloheptatrienes with covalent structure.



- Tropylium tetrafluoroborate salt is synthesied by the reaction of cycloheptatriene with triphenyl carbenium tetrafluoroborate.



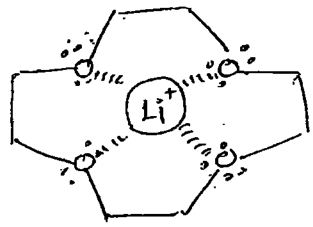
- Tropylium bromide salt is aromatic & strongly resonance stabilized. on removal of a hydride ion from CH_2 group of cycloheptatriene, a vacant p orbital is generated, & the carbon becomes sp^2 hybridized.
- The resulting tropylium ion has seven overlapping p orbitals with six delocalised π electrons. this situtation therefore makes tropylium cation an aromatic species.



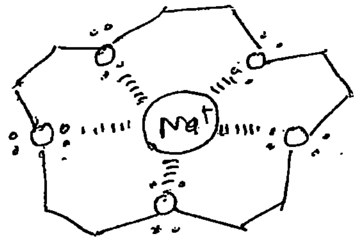
Inclusion compounds :-

- Inclusion complexes are formed when the host compound is capable to form a crystal lattice in which there are spaces which are of suitable size for the second compound (the guest) to fit.

- There is no bonding between the compounds acting as the host & guest but for the vander waals forces.
- For the successful formation of an inclusion compound, the guest molecule must fit into the space properly. In case the guest molecule is either too large or too small, will not go into the lattice & the addition compound will not form
- Urea is the most important host molecule for inclusion compound formations. Although ordinary crystalline urea is tetragonal, however in the presence of a suitable guest molecule it crystallizes in a hexagonal lattice with guest trapped in long channels.
- The diameter of the channel is about 5 Å, & the shape & size of the molecule determines if or not it can be a guest eg. octane & 1-bromooctane from complexes with urea while 2-bromooctane, 2-methyl heptane & 2-methyloctane are not suitable guests.
- The size & shape of the guest thus determines its entrance in the channels where it has to remain firmly in position.
- oleic acid gives erythro 9,10-dihydroxy steric acid (m.p. 132°) on syn hydroxylation. the threo isomer has (m.p. 95°). the configurational assignment to these diols was made on the basis of formation of a urea complex, while the erythro isomer does not.
- when one writes the staggered conformation of the two isomers it is the erythro diol in which the hydroxyl groups are on opposite side of



12-crown-4
chelates Li^+



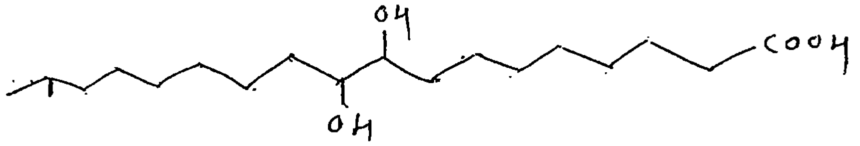
15- crown-5
chelates Na^+

- Thus 18-crown-6 binds K^+ (ionic diameter 2.66 Å) but not Li^+ (ionic diameter 1.20 Å), similarly 12-crown-4, binds Li^+ but not K^+.
- crown ethers have use in separating mixtures of cations & much use in organic synthesis.
- $KMnO_4$ with deep violet colour is completely insoluble solid in benzene, it however readily dissolves in benzene if 18-crown-6 is added to give a violet coloured solution. this solution is useful because it allows oxidations with $KMnO_4$ to be carried out in organic solvents.
- The solubility of $KMnO_4$ in benzene in the presence of 18-crown-6 is due the fact that six oxygen in 18-crown-6 are ideally situated to solvate a potassium cation.
- In the resulting complex the cation is solvated by the polar oxygens, but the exterior has hydrocarbon properties. As a result, the complexed ion is soluble in nonpolar solvents.

9 the chain. the Presence of these protruding groups Prevents entrance of the erythro diol into the urea channel.

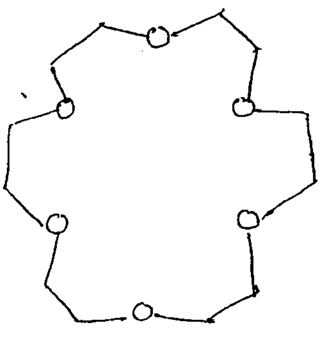
$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$

Oleic acid (cis isomer)

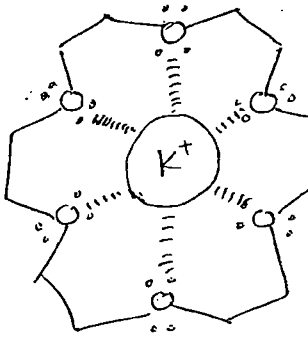


crown ether complexes :-

- crown ethers are large ring Polyethers. the compounds are cyclic Polymers of ethylene glycol, $(OCH_2CH_2)_n$, and are named in the form x-crown-y, where x is the total number of atoms in the ring and y is the number of oxygens.
- An example is 18-crown-6, the cyclic hexamer of ethylene glycol, crown ether are used as cheleting agents & are important for their Property of forming complexes with positive ions.
- Normally the cations are held tightly in the center of the cavity & each crown ether binds different ions depending on the size of the cavity. In each case the "cavity size" is a good match for the ionic diameter of the cation,



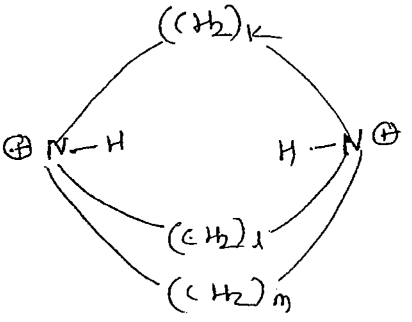
18-crown-6



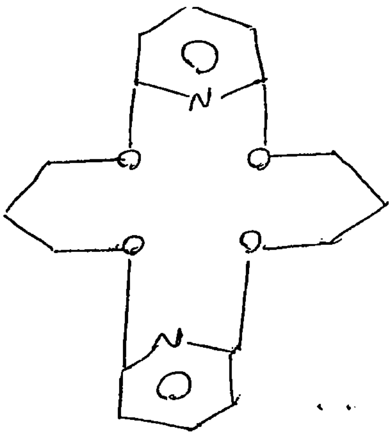
18-crown-6
chelates K+

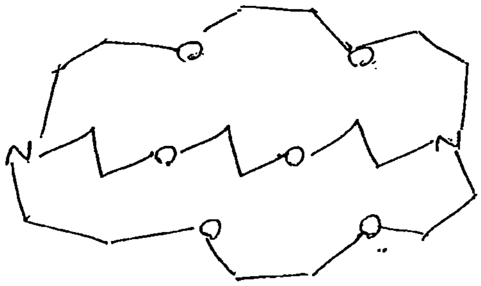
10. **Cryptands :—**

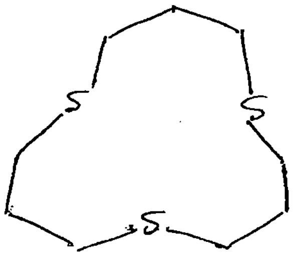
- macrocyclic systems related to crown ethers with nitrogen or sulfur atoms or more than one kind of hetero atom have been made.
- Bicyclic molecules bind the cations more tightly than monocyclic crown ethers. the bicyclic systems are named cryptands and the complexes with ions are termed cryptates. the mono-cyclic system are also often termed cryptands.
- Thus Bicyclic crown ethers (8) and crown ethers of cycles of higher order (tri, tetra --cycles) are called cryptands. ..
- Tricyclic cryptand (10) has ten binding sites & a spherical cavity & hence called spherand.
- In general, cryptands with their well defined three dimensional cavities, show additional & more pronounced ablity for complexation. these have been found to complex with anions also, e.g. the in-in isomer of 9, 9, 9 - tricyclic diamine salt (11) has a cavity large enough to encapsulate a chloride ion than is hydrogen bonded to the two N-H groups. the species thus formed is a cryptate having a negative rather than a positive ion enclosed.

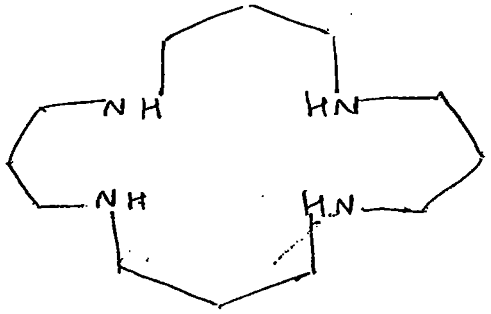


Both H are inside the ring



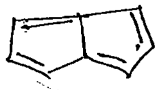


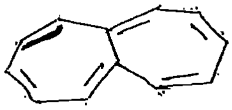


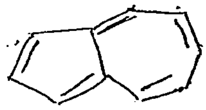


Azulene:-

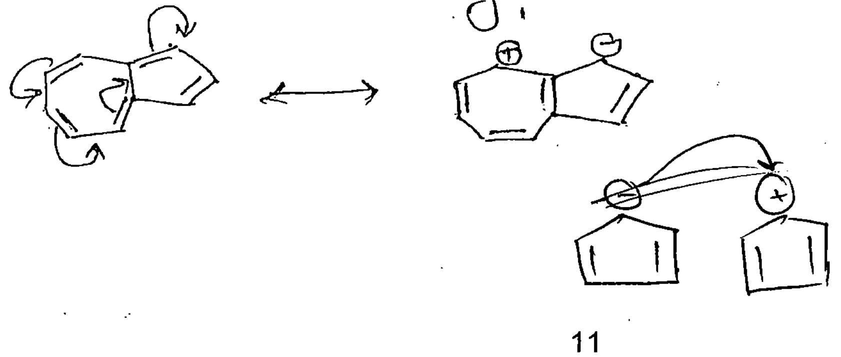
- Azulene is cyclic, planar. It has all sp^2 hybridised carbon atom.
- The aromatic system of electrons $(4n+2)$ can be spread over two rings only provided 10 electrons are available for aromaticity.
- Attempts to prepare pentalene & heptalene have failed since these do not contain $(4n+2)$ electron.
- Molecular orbital calculations show azulene to be stable compound while the other two are not. & this has been confirmed experimentally.
- Azulene has 1.0 D dipole moment while the dipole moment of the isomeric compound napthalene is zero.
- Azulene may be regarded as a combination of aromatic cyclopentadienyl anion & aromatic cycloheptatrienyl cation.


pentalene


Heptalene


Azulene

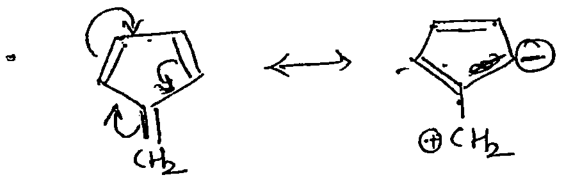
- In azulene electrophilic substitution reaction occur in five membered ring due to delocalization of electron. azulene is slightly dipolar & in five membered ring there is more electron density as compared to seven membered ring thus electrophilic substitution takes place in five membered ring.



~~Do not scan~~

Fulvene :-

- fulvene is cyclic and Planar.
- It also has all sp^2 orbitals for the atoms in the ring. it has six electron which is a huckel number but still it is nonaromatic because the $4n+2\pi$ electrons do not reside within the ring. moving the $C=CH_2$ π electrons into the ring results in the terminal carbon being electron deficient.

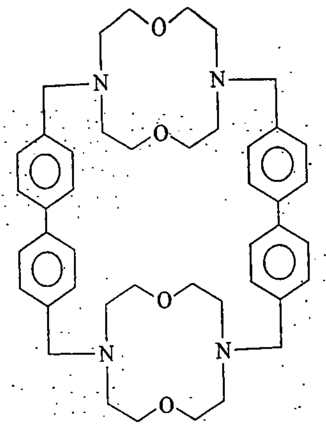


- The $C=C$ π bons of simple hydrocarbons are usually nucleophile, not electrophile. However when a nucleophile attacks the exocyclic carbon ~~atom~~ of the nonaromatic compound fulvene, the electron from the $C=C$ π bond go to the endo cyclic carbon & make the ring aromatic.

Non aromatic   Aromatic

ferrocene :-

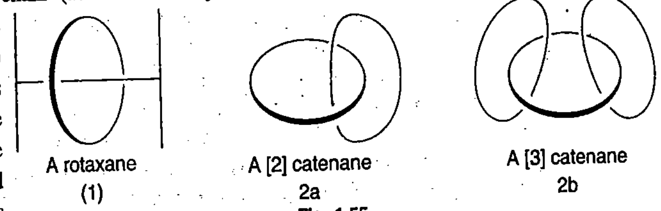
- ferrocene is Prepared by reacting cyclopentadienyl anions with ferrous ion Fe^{2+} in the ratio of 2:1 respectively, thus the grignard reagent of cyclopentadiene on reaction with ferrous chloride gives ferrocene as an orange solid.
- Ferrocene in one of many compounds with similar structure where one or more organic ions are



(12)

1.10 CATENANES AND ROTAXANES

There is very little free space in the centre of a cycloalkane unless the ring is quite large. Calculation indicates that cyclooctadecane is the smallest ring through which a —CH_2—$(CH_2)_n$—CH_2— chain (as linear or cyclic) can be threaded. Molecules have been synthesised that have large rings threaded on chains (1) and that have large rings which are interlocked like links in a chain (2). The former molecules are called rotaxanes and latter molecules are catenanes.



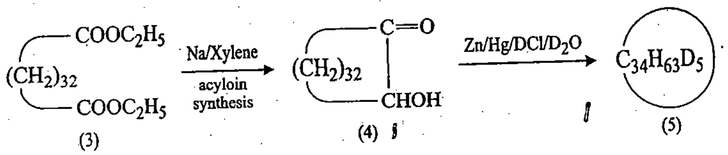
A rotaxane (1) A [2] catenane 2a A [3] catenane 2b

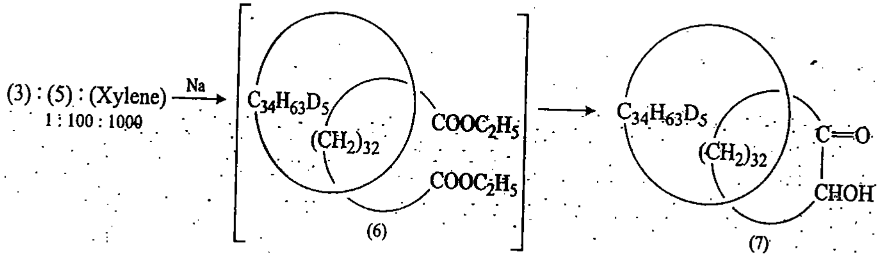
Fig. 1.55.

Thus **Catenanes** (Latin *catena* meaning chain) are molecules containing two or more intertwined rings. Similarly rotaxanes (from latin *rota* meaning wheel and axis) are molecules in which a linear molecule is threaded through a cyclic one and prevented from slipping out by large, bulky end-groups.

These two classes of compounds contain two or more portions that are not bonded to each other by any valence forces but neverthless must remain linked.

Catenanes and rotaxanes have been synthesised in two different ways. Statistical synthesis and directed synthesis. In a statistical synthesis of a catenane, a large ring is formed in the presence of another large ring. A finite number of chain molecules will, on a statistical basis, have become threaded through the ring before cyclisation. These threaded molecules, upon cyclisation of the chain give rise to a catenane (Scheme 1.10).

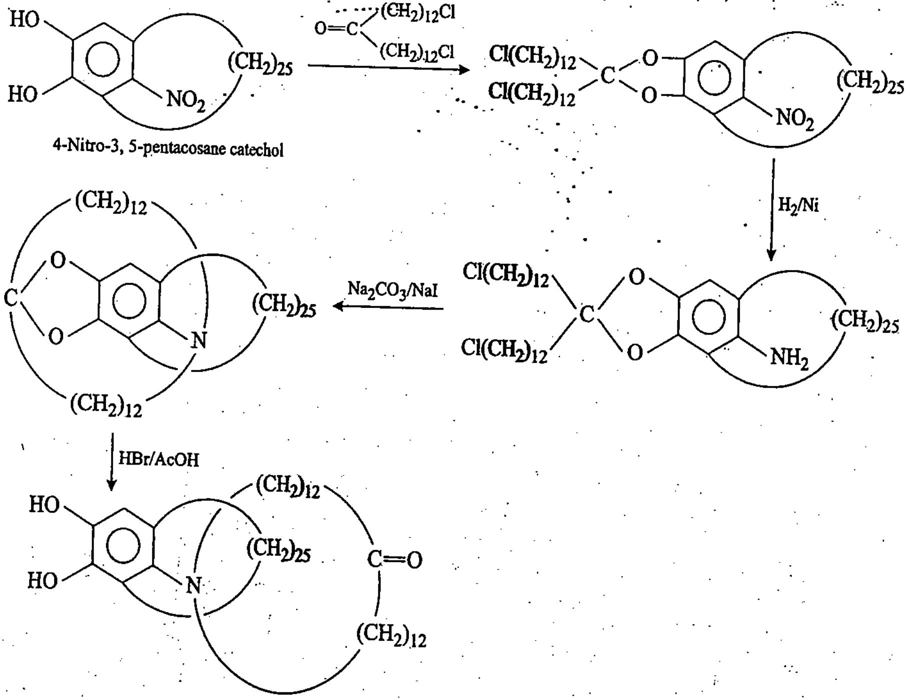




Scheme 1.10. Synthesis of [2] catenane, that is catenane with two interlocked rings.

1.10.1 Directed Synthesis of Catenanes

In this method the catenane forming subunits are designed in such a way that only cyclisation leading to the formation of catenane are possible (Scheme 1.11 and Scheme 1.12).



Scheme 1.11. Synthesis of [2] Catenane.

A template synthesis of a catenane has also been achieved (Scheme 1.13). The yield in this synthesis is 70%.

1.10.2 Synthesis of Rotaxanes

Statistical Synthesis : Statistical synthesis of a rotoxane is a reaction in which a compound **A** is bonded at two positions to another compounds **B** in the presence of large ring **C.** It is hoped that some **A** molecule would, by chance, be threaded through ring **C** before combining with the two then it will not trap iodine to give a blue colour. The general use of inclusion compounds falls into two main categories :

(1) Resolution of Mixtures :

(i) Removal of straight chain hydrocarbons present in petroleum through urea complexation from hydrocarbon mixture.

(ii) Removal of free fatty acids from oils or waxes by treatment with moist urea.

(iii) Separation of saturated and unsaturated fatty acids by urea adduct formation.

(iv) *cis-trans* iosmers can be separated by urea complexation.

(v) Benzene can be separated from the mixture of benzene and cyclohexane (both having very close boiling point) by treating the mixture with wet thiourea and filtering out the cyclohexane complex. The complex when shaken with water gives pure cyclohexane as water dissolves thiourea.

(2) Storage of Substances : Certain substances can be protected for a long time in the form of inclusion complexes. For example, auto-oxidation of oleic acid does not occur when the acid is in the form of urea complex.

The clathrates of inert gases provide a convenient method of dispersing the gases without restoring to high pressure cylinders.

Cyclodextrins

Cyclodextrins are oligosaccharides of glucose. A cyclodextrin consists of six, seven, eight or more D-glucose units joined through 1,4-*alpha* linkages in such a way as to form a ring—a chain bracelet each link of which is a pyranose hexagon. These rings are doughnut shaped, as much as crown ethers are, but with a number of important differences. The smallest of them, α-dextrin, has a diameter about double that of [18]-crown-6, and its hole (4·5 Å) is about double as broad. This hole is tapered slightly, so that the molecule is shaped like a tiny pail with the bottom knocked out (Fig. 1.59).

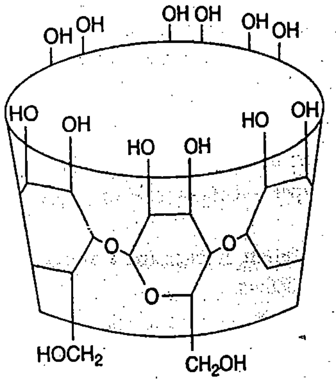
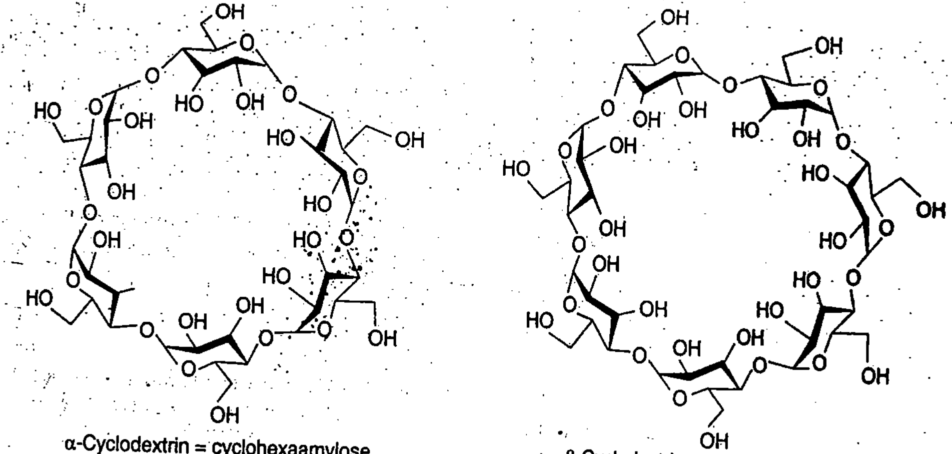


Fig. 1.59. A schematic representation of α-cyclodextrin. The secondary—OH groups face outward about the "upper" rim; the —CH$_2$OH groups face outward about the "lower" rim. The cavity is lined with C—H's and glycosidic O's in three bands lying one above another.

Making up the sides is a loop of six or more hexagons, each one lying roughly in the plane of the sides. Thus the depth of the pail is the width of the pyranose ring. Outside the pail, around the "upper" large rim lie the secondary —OH groups of C-2 and C-3; around the "lower" smaller rim lie the primary hydroxyl groups of C-6. The inside of the pail consists of three bands, one on top of another; two bands of C—H's in between, a band of glycosidic O's.

Dextrin having six glucose units is known as α-dextrin. Dextrins having seven and eight glucose units are known as β and γ-dextrins, respectively (Figs. 1.60 and 1.61).



α-Cyclodextrin = cyclohexaamylose

β-Cyclodextrin = cycloheptaamylose

Fig. 1.60.

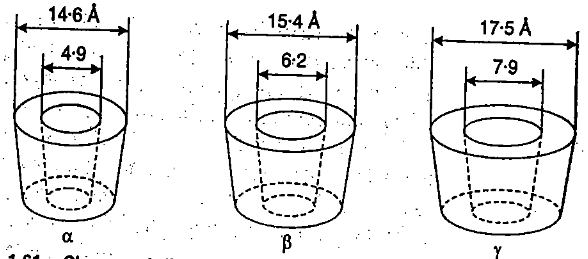


Fig. 1.61. Shape and dimensions of the α-, β-, and γ-cyclodextrin molecules.

Like a crown ether, a cyclodextrin can act as host to guest molecules. Guest molecules are aromatics, halogens, and fatty acids. Dextrins form channel type inclusion compounds as well as cage complexes. In contrast to crown ethers, a cyclodextrin has a polar hydrophilic outside and a relatively non-polar lipophilic inside. This leads naturally to two important results :

(i) into its lipophilic interior a cyclodextrin typically takes as non-polar organic molecule or the non-polar end of an organic molecule as a guest, and

(ii) its hydrophilic exterior confers water solubility on the resulting inclusion complex. How well a guest molecule is accommodated depends upon its size and polarity, and the size of the particular cyclodextrin. (Table 1).

Table 1 : Characteristics of cyclodextrins.

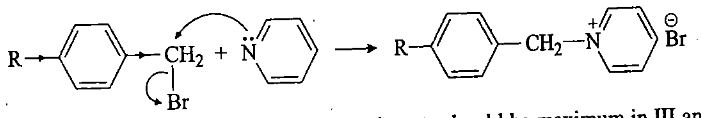
Cyclodextrin	Glucose unit per ring	Channel diameter (Å)	Guests
α	6	6	halogens, aliphatics, benzene derivatives with small substituents
β	7	8	Br_2, I_2, organics
γ	8	10–17	I_2, only large organics

For example, bromobenzene is too large to fit into the α-dextrin and does not form an inclusion compound, but it does form a compound with the β- or γ-cyclodextrins. There is a similar trend with the halogens. The cyclodextrins also form inclusion compounds in solution, this accounts for the blue colour formed by iodine and starch solution.

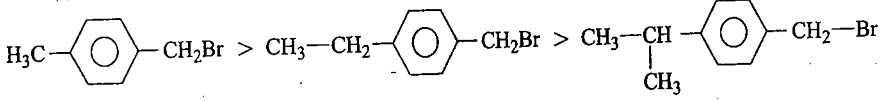
Cyclodextrins can be used to catalyse organic reactions often with regioselectivity.

PROBLEMS WITH SOLUTIONS

1. Resonance energy of benzene is much more higher than 1,3-butadiene. Why?
2. 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.
3. Carbon-nitrogen bond length in methylamine is 0·147 nm whereas this bond length in urea is only 0·137 nm. Explain.
4. The dipole moment of nitrobenzene (μ = 3·95 D) is higher than nitromethane (μ = 3·60 D) although both have same polar group. Why?
5. Baker and Nathan examined the rates of reaction of *p*-alkyl substituted benzyl bromides towards pyridine in acetone medium; the reaction is supposed to follow the SN2 pathway : They observed the following rate order :

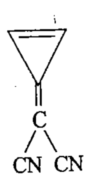


According to the mechanism proposed by them the rate should be maximum in III and minimum in (I). How the observed rate can be explained?

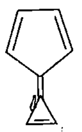


(I) > (II) > (III)

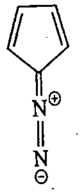
6. The given compounds are aromatics or non-aromatics and why? Explain.



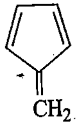
(I)



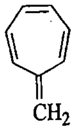
(II)



(III)



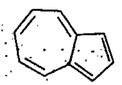
(IV)



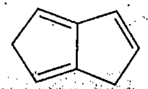
(V)

7. 7-Bromocycloheptatriene completely dissociates in water and gives a precipitate of AgBr with $AgNO_3$, unlike its open-chain analogue, 3-bromo-1,4-pentadiene. Explain.
8. Explain why cyclopentadiene is much more acidic than 1,3-cyclohexadiene.
9. Explain why cycloheptatriene is much less acidic than a typical allylic compounds.

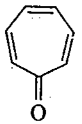
10. Azulene ($C_{10}H_8$) is a deep-blue compound with the structure shown below : Account for its aromaticity and its dipole moment (μ = 1·0 D).



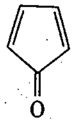
11. Define mesoionic compounds? Explain the aromaticity of sydnones.
12. Cyclooctatetraene adds two electrons when treated with potassium metal and forms a stable, planar dianion $C_8H_8^{2-}$. Use the molecualr orbital diagram and explain its stability.
13. Phenyllithium removes two hydrogens as protons from the given compound. The dianion obtained in this process is stable. Provide an explanation for the stability of dianion.



14. Cycloheptatrione (A) is very stable. Cyclopentadienone (B) by contrast is quite unstable and rapidly undergoes a Diels-Alder reaction with itself. Propose an explanation for the different stabilities of these two compounds.



(A)



(B)

15. Explain why a substitutent such as nitro bonded to *ortho* or *para* position has a much greater effect on the acidity of a phenol than a benzoic acid.
16. In terms of *s*-character, which nitrogen of guanidine is more likely to be protonated? Also account for the fact that guanidine is a strong base ($Kb = 1$).
17. Account for the fact that (i) 4-cyanoaniline is slightly more basic than 4-nitroaniline and (ii) 3,4,5-trinitroaniline is mroe basic than 4-cyanoaniline.

PROBLEMS for SELF ASSESSMENT

1. With the help of π molecular orbitals of annulenes, explain why annulenes having (4n + 2) π electrons are more stable than the one containing (4n) π electrons.
2. With potassium in liquid ammonia, aromatic annulenes undergo one electron reduction but COT shows two electron reduction. Comment.
3. Give brief account of the following :
   (i) Alternant and non-alternant hydrocarbons.
   (ii) Hyperconjugation.
   (iii) Resonance energy.
4. Explain aromaticity on the basis of perturbation molecular orbital theory.
5. What are antiaromatic and homoaromatic compounds? Give examples of these.
6. With the help of π-molecular orbital energy diagram, explain why benzene is more stable than cyclobutadiene.
7. Discuss aromaticity of non-benzenoid aromatic compounds.