1. Learning Outcomes

After studying this module, you shall be able to understand:

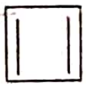
- What are annulenes?
- How can you synthesize annulenes?
- What are the reactions possible of annulenes?

2. Introduction

Annulenes are completely conjugated monocyclic hydrocarbons. They have a general formula C_nH_n. According to the IUPAC naming conventions, annulenes are named as [*n*]-annulene, where *n* is the number in the bracket indicates the ring size or the number of carbon atoms in their ring.

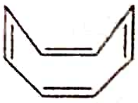
For example,

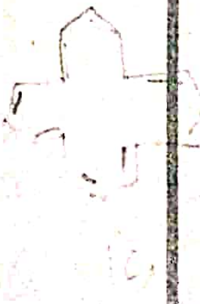
Cyclobutadiene is named as [4]-annulene,
Benzene is named as [6]-annulene,
Cyclooctatetraene is named as [8]-annulene,
Cyclodecapentaene is named as [10]-annulene,
Cyclododecahexaene is named as [12]-annulene,
Cyclotetradecaheptaene named as [14]-annulene,
Cyclohexadecaheptaene named as [16]-annulene,
Cyclooctadecanonaene named as [18]-annulene and so on. The structures are given below:

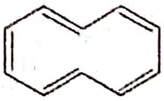

[4] Annulene
Not aromatic

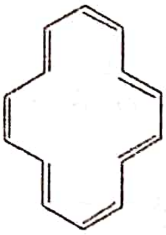

[6] Annulene
Aromatic

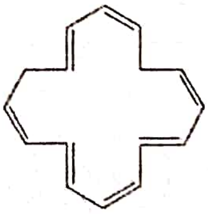

[8] Annulene (planar)
Not aromatic

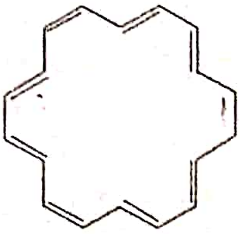

[8] Annulene (Tub shaped)
Aromatic




[10] Annulene
Not aromatic


[14] Annulene
Aromatic

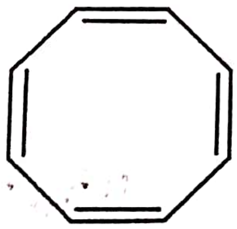

[16] Annulene
Nonromatic

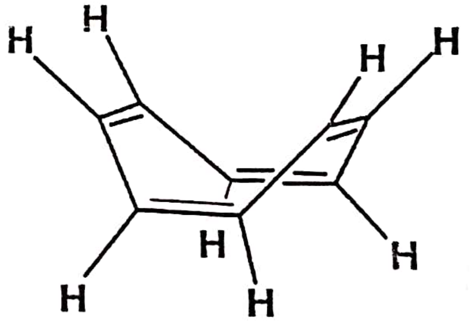

[18] Annulene
Aromatic

Annulenes were first prepared by Sondheimer et al in 1962 to test the Huckel's rule of aromaticity. According to Huckel's rule of aromaticity 'if the number of π-electrons is equal to $4n+2$ where n is equal to zero or a whole number, the system is aromatic'. The number of π-electrons for Hückel's rule are 2 (n = 0), 6 (n = 1), 10 (n = 2), 14 (n = 3), 18 (n = 4) etc. Various annulenes prepared were have n= 10, 12, 14, 16, 18, 20, 24, 30. Out of these only [14], [18], [30] annulenes have $(4n + 2)$ π-electrons and are aromatic in nature.

The [4]-annulene is cyclobutadiene having 4π-electrons and is anti-aromatic in nature. It is highly unstable due to the ring strain. It can be isolated only under controlled conditions like in Argon matrix or using trapping agents like dienes. Studies show that it has a rectangular structure rather than a square, with C-C bond length of 1.567 Å and C=C bond length of 1.346 Å.

The [8]-annulene is also known as cyclooctatetraene. It is a polyunsaturated hydrocarbon, which is a colorless to light yellow flammable liquid at room temperature. It is non-planar and adopts a tub-conformation as shown below:





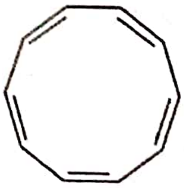
The [10]- and [14]-annulene are not particularly stable due to geometric factors. [10] Annulene is also known as cyclodecapentaene. Since it has conjugated 10-π electrons but still it is not aromatic due to the combination of steric strain and angular strain. Many conformations are possible for [10] annulene:

(1) **Planar all-*cis* isomer:** in this conformation all the bond angles are of 144° which creates large amounts of bond strain relative to the ideal 120° for sp^2 hybridization,

(2) **Boat-like all-*cis* conformation:** In this conformation angular strain is less in comparison to (1) but is still unstable,

(3) **Planar *trans, cis, trans, cis, cis* isomer:** This conformation suffers from steric repulsion between the two internal hydrogen atoms,

(4) **Non-planar *trans, cis, cis, cis, cis* isomer:** This is the most stable of all the possible isomers.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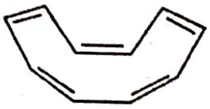
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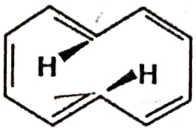
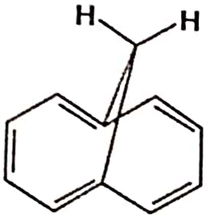


3


4



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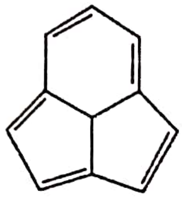
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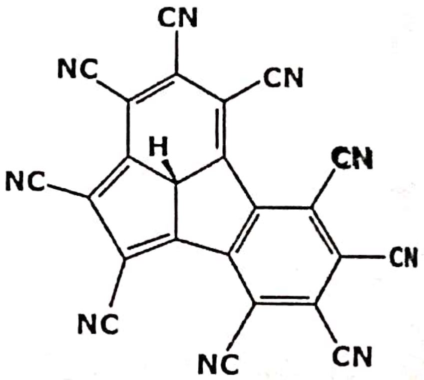


7

The [14] annulene has 14 electrons in its conjugated pi system and hence it possess some aromatic character. The [16]-annulene is non-planar, with alternating C=C and C-C like a non-aromatic polyene. The [18]-annulene is almost planar, with some aromatic stability. However, it reacts more like a polyene than benzene. It undergoes addition reaction with H_2 and Br_2, and a Diels-Alder with maleic anhydride. The higher annulenes ($n > 18$) are of less synthetic interest. This is mostly due to their significant bond alternation asymmetry, and conformational flexibility. All the higher annulenes up to $n = 30$ have been synthesized except $n = 26$ and 28.

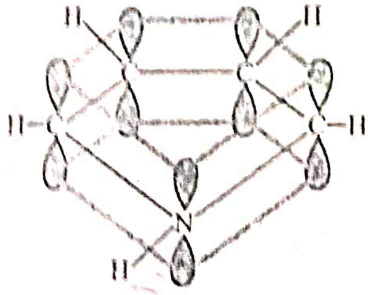
3. Synthesis of annulenes

3.1 Synthesis of [4]-annulene

Cyclobutadiene was first synthesized in 1965 by Rowland Pettit et al although they could not isolate it. In 1965, the first stable pale yellow crystalline solid cyclobutadieneiron tricarbonyl was prepared from $Fe_2(CO)_9$ and *cis*-dichlorocyclobutene *via* double dehydrohalogenation reaction.

5. Summary

- Annulenes are conjugated monocyclic hydrocarbons with a general formula C_nH_n.
- According to the IUPAC naming conventions, annulenes are named as [*n*]-annulene, where *n* is the number in the bracket indicates the ring size or the number of carbon atoms in their ring.
- Some annulenes possess aromatic character while others are non-aromatic polyene.
- The higher annulenes ($n > 18$) are of less synthetic interest. This is mostly due to their significant bond alternation asymmetry, and conformational flexibility.
- The synthesis of selected annulenes are discussed like synthesis of [4]-annulene, [8]-annulene; [10]-annulenes and [18]-annulenes.
- The [8]-aanulenes can easily be synthesized by Richard Willstatter synthesis and Reppe's synthesis.
- The important reactions of [4]-annulenes, [6]-annulenes, [10]-annulenes and [18]-annulenes have been discussed



33

HETEROCYCLIC COMPOUNDS-I

33.0. INTRODUCTION

Heterocyclic compounds are relatively **stable ring** compounds in which *one* or *more* of the ring atoms are of elements other than carbon called **hetero** *atom* (s) (*Hetero*-different). These hetero atoms are mostly N, O and S. Elements like P, B, Si, Sn, Al, As, Cu are also occasionally incorporated in the ring. Epoxides (*e.g.*, ethylene oxide) and lactones (*e.g.*, γ-butyrolactone) are generally excluded due to the relative instability of their ring systems.

Their names may be given after the hetero atoms present in the ring. Thus we have **oxygen heterocyclics** like *furan*, *pyran*, *etc.*, **nitrogen heterocyclics** like *pyrrole*, *pyridine*, *piperidine*, *etc.*, **sulphur heterocyclics** like *thiophene*, *thiopyran*, *etc.* for single *hetero atom* containing compounds.

They may also be classified on the basis of the *size* of the heterocyclic ring present. We have for example, **5-membered heterocyclics** (Furan, pyrrole thiophene *etc.*); **6-membered heterocyclics** (pyridine, piperidine, pyran, thiopyran *etc.*); containing ***single*** **hetero** atom.

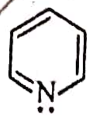
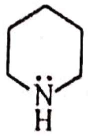
Five membered rings containing single heteroatom :





Common name	**Pyrrole**	**Furan**	**Thiophene**	**Tetrahydrofuran**	**Pyrrolidine**
IUPAC name	*Azole*	*Oxole*	*Thiole*	*Oxolane*	*Azolidine*

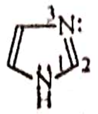
Six membered rings containing single heteroatom :

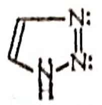



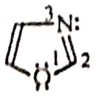

Common name	**Pyridine**	**Piperidine**	**γ-Pyran**	**γ-Thiopyran**	**Tetrahydropyran**
IUPAC name	*Azine*	*Perhydrazine*	*4H-Oxane*	*4H-Thiane*	*Oxane*

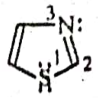
Five membered rings containing two or more hetero atoms :

The suffix-***azole*** is used for five membered rings containing two or more hetero atoms with atleast one nitrogen atom. For example,





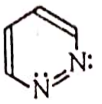


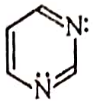


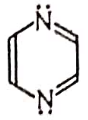
Common name	Pyrazole	Imidazole	1, 2, 3,-Triazole	Oxazole	Thiazole
IUPAC name	*1,2-Diazole*	*1,3-Diazole*		*1,3-Oxazole*	*1,3-Thiazole*

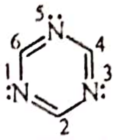
Six membered rings containing two or more hetero atoms :

The suffix-***azine*** is used for six membered rings containing **two or more hetero** atoms. For example,





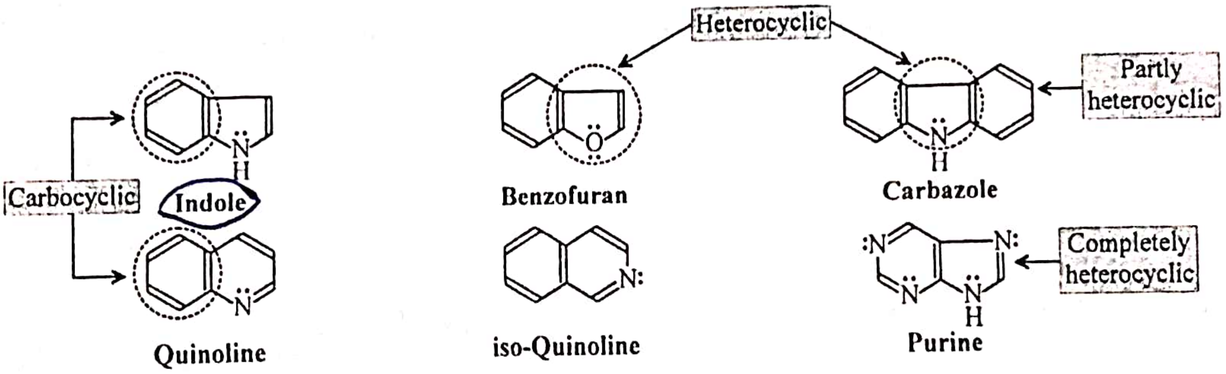




Common name	Pyridazine	Pyrimidine	Pyrazine	sym-Triazine
IUPAC name	*1,2-Diazine*	*1,3-Diazine*	*1,4-Diazine*	*1,3,5-Triazine*

Condensed heterocyclics.

Occasionally, we have **condensed heterocyclics** containing *two* or *more* fused rings. The 'fused' rings may be partly *carbocyclic* and partly *heterocyclic* (*e.g.*, indole, benzofuran, carbazole, quinoline, isoquinoline, *etc.*) or *completely heterocyclic* (*e.g.*, purine).



Recently, heterocyclic compounds have been given class names which symbolise their chemical behaviour. ***Heteroparaffins*** (*e.g.*, pyrrolidine, tetrahydrofuran, piperidine, *etc.*) resemble to ***paraffins*** whereas *heteroaromatics* (*e.g.*, pyrrole, furan, thiophene, pyridine, *etc.*) resemble to ***aromatics***.

33.1. NOMENCLATURE

(1) The *systematic* names for monocyclic compounds are given by using prefixes for the nature of hetero atom(s) present and dropping 'a' whenever necessary; *e.g.*, ***oxa***- (for oxygen); ***thia***- (sulphur); ***aza***- (nitrogen), ***sila***- (silicon) and ***phospha***- (phosphorus), *etc.* If *two* or *more similar* hetero atoms are present, the prefixes ***di-***, ***tri*** - *etc.* are used, *e.g.*, **triaza**, **trioxa**, *etc.* If hetero atoms are *different the numbering starts from hetero atom of the highest group in the periodic table and as low an atomic number when in the same group.* Thus the order of naming will be O, S, N, P, Si, *etc. e.g.*, oxaza (O then N).

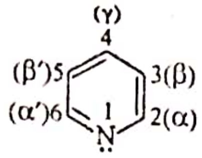
(2) The *size* of the monoheterocyclics is indicated by **suffix-*ole*** for 5-membered and - ***ine*** for six membered.

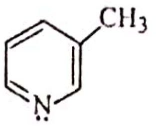
(3) In monoheterocyclics numbering is given in such a way that the ***hetero atom*** gets the ***lowest***

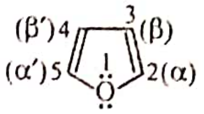
number and proceeds in ***anticlockwise*** around the ring.

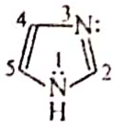
(4) When the *hetero atoms* are *different*, the numbering is given in according to the order given in rule-1, and proceed round the ring in order of precedence.

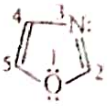
(5) In common names ***Greek letters*** denote the position of the substituents. For example,





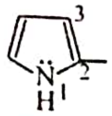




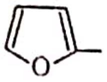


Common name	Pyridine	β-Methylpyridine	Furan	Imidazole	Oxazole
IUPAC name	*Azine*	*3-Methylazine*	*Oxole*	*1, 3-Diazole*	*1, 3-Oxazole*

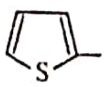
The radicals derived from pyrrole, furan and thiophene by the replacement of one hydrogen are known as ***pyrryl-***, ***furyl-***and ***thienyl-***respectively. The position of hydrogen replaced is indicated by the number assigned to that carbon. For example,



2-Pyrryl-



2-Furyl-

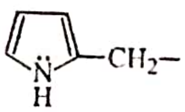


2-Thienyl

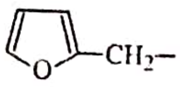
3-Thienyl-

3-Furyl-

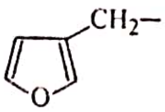
The radicals derived from the corresponding methyl derivatives by the replacement of hydrogen are known as ***pyrrolyl-***, ***furfuryl-*** and ***thenyl***. For example,



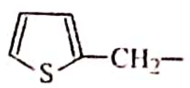
2-Pyrrolyl-



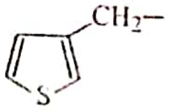
2-Furfuryl-



3-Furfuryl-

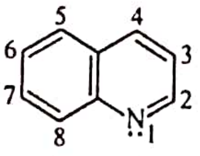


2-Thenyl-

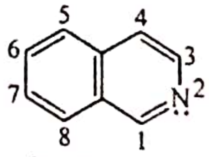


3-Thenyl-

Exception. 'N' does not get the lowest number in iso-quinoline, here the numbering is followed in accordance to quinoline structure, see below.



Quinoline



***iso*-Quinoline**

I. FIVE-MEMBERED HETEROCYCLES

33.2. OCCURRENCE

Pyrrole, *furan* and *thiophene* are the three simple five-membered heterocyclics. Pyrrole occurs in coal tar whereas furan is present in pine wood. Thiophene occurs in coal tar and shale oil. Naturally occuring compounds like chlorophyll, haemin, cyanocobalamine (vit. B_{12}), auxins, alkaloids, etc. contain ***pyrrole*** ring system.

33.3. GENERAL METHOD OF FORMATION (Paal Knorr Synthesis)

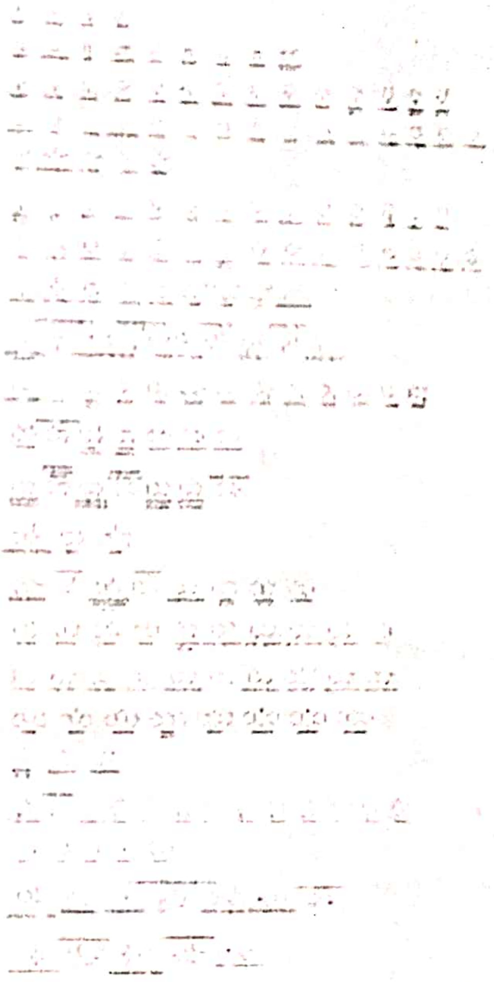
A general synthesis for *pyrrole*, *furan* and *thiophene* derivatives can be achieved from,

I. M.Sc. Chemistry.

Heterocyclic compound

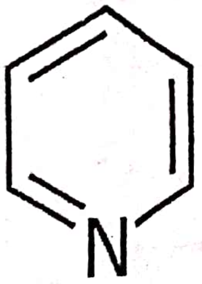
A **heterocyclic compound** or **ring structure** is a cyclic compound that has atoms of at least two different elements as members of its ring(s).[1] **Heterocyclic chemistry** is the branch of organic chemistry dealing with the synthesis, properties, and applications of these **heterocycles**.[2]

Examples of heterocyclic compounds include all of the nucleic acids, the majority of drugs, most biomass (cellulose and related materials), and many natural and synthetic dyes.



structures and names of common and not so common heterocycle compounds

Contents



Pyridine, a heterocyclic compound

Classification

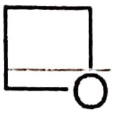
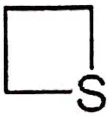
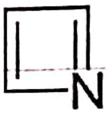
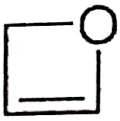
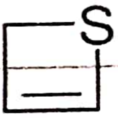
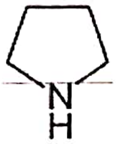
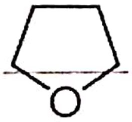
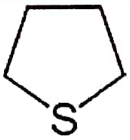
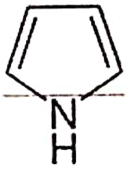
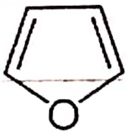
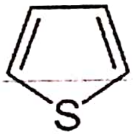
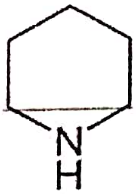
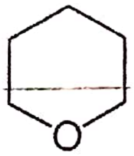
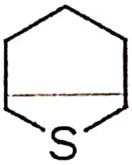
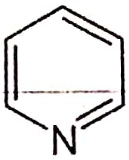
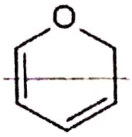
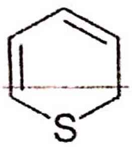
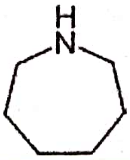
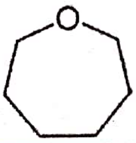
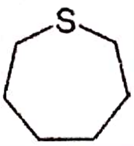
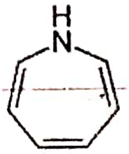
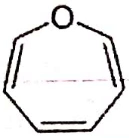
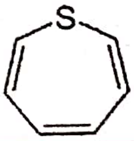
Although heterocyclic chemical compounds may be inorganic compounds or organic compounds, most contain at least one carbon. While atoms that are neither carbon nor hydrogen are normally referred to in organic chemistry as heteroatoms, this is usually in comparison to the all-carbon backbone. But this does not prevent a compound such as borazine (which has no carbon atoms) from being labelled "heterocyclic". IUPAC recommends the Hantzsch-Widman nomenclature for naming heterocyclic compounds.

Heterocyclic compounds can be usefully classified based on their electronic structure. The saturated heterocycles behave like the acyclic derivatives. Thus, piperidine and tetrahydrofuran are conventional amines and ethers, with modified steric profiles. Therefore, the study of heterocyclic chemistry focuses especially on unsaturated derivatives, and the preponderance of work and applications involves unstrained 5- and 6-membered rings. Included are pyridine, thiophene, pyrrole, and

Heteroatom	Saturated	Unsaturated
Nitrogen	Azonane	Azonine
Oxygen	Oxonane	Oxonine
Sulfur	Thionane	Thionine

Images

Names in italics are retained by IUPAC and they do not follow the Hantzsch-Widman nomenclature

	Saturated			Unsaturated		
Heteroatom	**Nitrogen**	**Oxygen**	**Sulfur**	**Nitrogen**	**Oxygen**	**Sulfur**
3-Atom Ring	Aziridine	Oxirane	Thiirane	Azirine	Oxirene	Thiirene
						
4-Atom Ring	Azetidine	Oxetane	Thietane	Azete	Oxete	Thiete
						
5-Atom Ring	*Pyrrolidine*	Oxolane	Thiolane	*Pyrrole*	*Furan*	*Thiophene*
						
6-Atom Ring	*Piperidine*	Oxane	Thiane	*Pyridine*	*Pyran*	*Thiopyran*
						
7-Atom Ring	Azepane	Oxepane	Thiepane	Azepine	Oxepine	Thiepine
						

Fused rings

Heterocyclic rings systems that are formally derived by fusion with other rings, either carbocyclic or heterocyclic, have a variety of common and systematic names. For example, with the benzo-fused unsaturated nitrogen heterocycles, pyrrole provides indole or isoindole depending on the orientation. The pyridine analog is quinoline or isoquinoline. For azepine, benzazepine is the preferred

- ## Five-membered rings with*one* heteroatom

Heteroatom	Saturated	Unsaturated
Antimony	Stibolane	Stibole
Arsenic	Arsolane	Arsole
Bismuth	Bismolane	Bismole
Boron	Borolane	Borole
Nitrogen	*Pyrrolidine* (Azolidine is not used)	*Pyrrole* (Azole is not used)
Oxygen	*Tetrahydrofuran*	*Furan*
Phosphorus	Phospholane	Phosphole
Selenium	Selenolane	Selenophene
Silicon	Silacyclopentane	Silole
Sulfur	Tetrahydrothiophene	*Thiophene*
Tin	Stannolane	Stannole

Five-membered rings with*two* heteroatoms

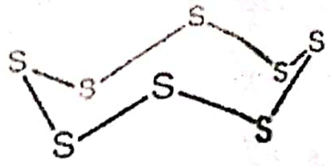
The 5-membered ring compounds containing *two* heteroatoms, at least one of which is nitrogen, are collectively called the azoles. Thiazoles and isothiazoles contain a sulfur and a nitrogen atom in the ringDithiolanes have two sulfur atoms.

Heteroatom	Saturated	Unsaturated (and partially unsaturated)
Nitrogen/nitrogen	*Imidazolidine* *Pyrazolidine*	*Imidazole* (Imidazoline) *Pyrazole* (Pyrazoline)
Nitrogen/oxygen	Oxazolidine Isoxazolidine	Oxazole (Oxazoline) Isoxazole
Nitrogen/sulfur	Thiazolidine Isothiazolidine	Thiazole (Thiazoline) Isothiazole
Oxygen/oxygen	Dioxolane	
Sulfur/sulfur	Dithiolane	

Five-membered rings with at least*three* heteroatoms

A large group of 5-membered ring compounds with *three* heteroatoms also exists. One example is dithiazoles that contain two sulfur and a nitrogen atom.

furan. Another large class of heterocycles are fused to benzene rings, which for pyridine, thiophene, pyrrole, and furan are quinoline, benzothiophene, indole, and benzofuran, respectively. Fusion of two benzene rings gives rise to a third large family of compounds, respectively the acridine, dibenzothiophene, carbazole, and dibenzofuran. The unsaturated rings can be classified according to the participation of the heteroatom in the conjugated system, pi system.



cyclo-Octasulfur, a homocyclic compound

3-membered rings

Heterocycles with three atoms in the ring are more reactive because of ring strain. Those containing one heteroatom are, in general, stable. Those with two heteroatoms are more likely to occur as reactive intermediates.

Common 3-membered heterocycles with *one* heteroatom are:

Heteroatom	Saturated	Unsaturated
Boron	Borirane	Borirene
Nitrogen	Aziridine	Azirine
Oxygen	Oxirane (ethylene oxide, epoxides)	Oxirene
Phosphorus	Phosphirane	Phosphirene
Sulfur	Thiirane (episulfides)	Thiirene

Those with *two* heteroatoms include:

Heteroatom	Saturated	Unsaturated
Nitrogen	Diaziridine	Diazirine
Nitrogen/oxygen	Oxaziridine	
Oxygen	Dioxirane	

4-membered rings

Compounds with one heteroatom:

Heteroatom	Saturated	Unsaturated
Nitrogen	Azetidine	Azete
Oxygen	Oxetane	Oxete
Sulfur	Thietane	Thiete

Compounds with two heteroatoms:

Heteroatom	Saturated	Unsaturated
Nitrogen	Diazetidine	Diazete
Oxygen	Dioxetane	Dioxete
Sulfur	Dithietane	Dithiete

5-membered rings

With heterocycles containing five atoms, the unsaturated compounds are frequently more stable because of aromaticity.

Heteroatom	Saturated	Unsaturated
3 × Nitrogen		Triazoles
2 × Nitrogen / 1 × oxygen		Furazan Oxadiazole
2 × Nitrogen / 1 × sulfur		Thiadiazole
1 × Nitrogen / 2 × oxygen		Dioxazole
1 × Nitrogen / 2 × sulfur		Dithiazole
4 × Nitrogen		Tetrazole
4 × Nitrogen/1 × Oxygen		Oxatetrazole
4 × Nitrogen/1 × Sulfur		Thiatetrazole
5 × Nitrogen		Pentazole

6-membered rings

Six-membered rings with a *single* heteroatom:

Heteroatom	Saturated	Unsaturated
Antimony		Stibinin[3]
Arsenic	Arsinane	Arsinine
Bismuth		Bismin[4]
Boron	Borinane	Borinine
Germanium	Germinane	Germine
Nitrogen	*Piperidine* (Azinane is not used)	*Pyridine* (Azine is not used)
Oxygen	Tetrahydropyran	*Pyran* (2*H*-Oxine is not used)
Phosphorus	Phosphinane	Phosphinine
Silicon	Silinane	Siline
Sulfur	Thiane	*Thiopyran* (2*H*-Thiine is not used)
Tin	Stanninane	Stannine

With *two* heteroatoms:

Heteroatom	Saturated	Unsaturated
Nitrogen / nitrogen	*Piperazine*	Diazines
Oxygen / nitrogen	*Morpholine*	Oxazine
Sulfur / nitrogen	*Thiomorpholine*	Thiazine
Oxygen / oxygen	Dioxane	Dioxine
Sulfur / sulfur	Dithiane	Dithiin

With three heteroatoms:

Heteroatom	Saturated	Unsaturated
Nitrogen	Hexahydro-1,3,5-triazine	Triazine
Oxygen	Trioxane	
Sulfur	Trithiane	

With four heteroatoms:

Heteroatom	Saturated	Unsaturated
Nitrogen		Tetrazine

With five heteroatoms:

Heteroatom	Saturated	Unsaturated
Nitrogen		Pentazine

The hypothetical compound with six nitrogen heteroatoms would be hexazine.

7-membered rings

With 7-membered rings, the heteroatom must be able to provide an empty pi orbital (e.g., boron) for "normal" aromatic stabilization to be available; otherwise, homoaromaticity may be possible. Compounds with one heteroatom include:

Heteroatom	Saturated	Unsaturated
Boron		Borepin
Nitrogen	Azepane	Azepine
Oxygen	Oxepane	Oxepine
Sulfur	Thiepane	Thiepine

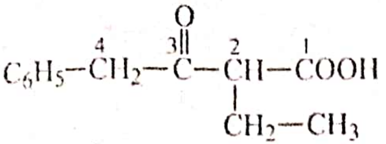
Those with two heteroatoms include:

Heteroatom	Saturated	Unsaturated
Nitrogen	Diazepane	Diazepine
Nitrogen/sulfur		Thiazepine

8-membered rings

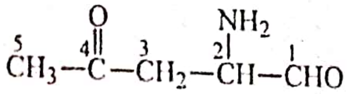
Heteroatom	Saturated	Unsaturated
Nitrogen	Azocane	Azocine
Oxygen	Oxocane	Oxocine
Sulfur	Thiocane	Thiocine

9-membered rings

(18) 

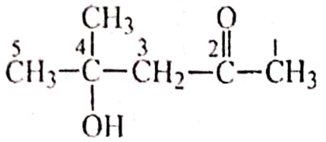
$\overset{4}{C_6H_5-CH_2}-\overset{\overset{O}{\|}}{\overset{3}{C}}-\underset{\underset{CH_2-CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}OOH$

2-Ethyl-3-oxo-4-phenylbutanoic acid

(19) 

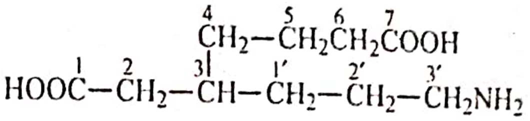
$\overset{5}{C}H_3-\overset{\overset{O}{\|}}{\overset{4}{C}}-\overset{3}{C}H_2-\overset{\overset{NH_2}{|}}{\overset{2}{C}H}-\overset{1}{C}HO$

2-Amino-4-oxopentanal

(20) 

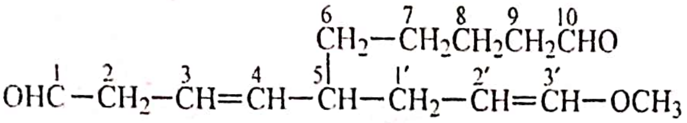
$\overset{5}{C}H_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{\overset{4}{C}}}-\overset{3}{C}H_2-\overset{\overset{O}{\|}}{\overset{2}{C}}-\overset{1}{C}H_3$

4-Hydroxy-4-methyl-2-pentanone

(21) 

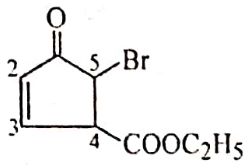
$HOO\overset{1}{C}-\overset{2}{C}H_2-\overset{\overset{\overset{4}{C}H_2-\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}OOH}{|}}{\overset{3}{C}H}-\overset{1'}{C}H_2-\overset{2'}{C}H_2-\overset{3'}{C}H_2NH_2$

3-(3′-Aminopropyl)-heptanedioic aicd

(22) 

$OH\overset{1}{C}-\overset{2}{C}H_2-\overset{3}{C}H=\overset{4}{C}H-\overset{\overset{\overset{6}{C}H_2-\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_2\overset{10}{C}HO}{|}}{\overset{5}{C}H}-\overset{1'}{C}H_2-\overset{2'}{C}H=\overset{3'}{C}H-OCH_3$

5-(3′-Methoxy-2′-propenyl)-3-decenedial

(23) 

5-Bromo-4-carbethoxycyclopent-2en-1-one

(24) $HOO\overset{1}{C}-\overset{2}{C}H_2-\overset{3}{C}H=O$

3-Oxo-propanoic acid

[In example 23, the functional group constituting the **ring** system is given priority over to ester group present in side chain as carbethoxy substituent]

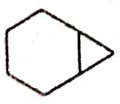
5.8. IUPAC NOMENCLATURE OF BICYCLIC COMPOUNDS

These compounds derive their names from the considerations of bicylic structures. All such compounds have two structural features in common

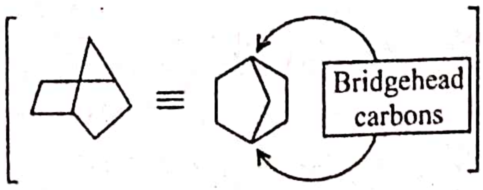
(*i*) *Two* bridgehead carbon atoms

(*ii*) *Three* arms connecting the two bridgehead carbon atoms.

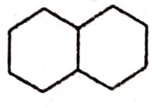
These compounds are named as derivatives of alkanes corresponding to the *total number of carbons in both ring* system. The term **bicyclo** is used as ***prefix*** together with the *numbers of carbons in each* of the *three connecting arms* inserted *in brackets*. For example,



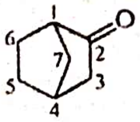
Bicyclo[4.1.0] heptane



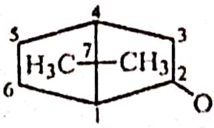
Bicyclo[2.2.1]heptane



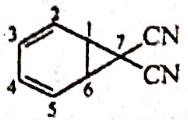
Bicyclo[4.4.0]decane



Bicyclo [2.2.1] haptan-2-*one*



7, 7-Dimethylbicyclo[2.2.1]heptan-2-ol

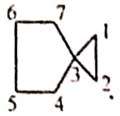


7, 7-Dicyanobicyclo[4.1.0]hepta-2, 4-diene

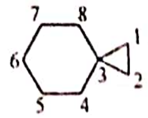
The numbering used to assign substitutents or functional groups *begins from* the *bridgehead position*, proceeds along the *longest* arm to the other bridgehead, and continues along the *next longest arm*. The bridgehead position selected is one that is *close to the carbon bearing functional group* or substituent as shown above.

5.4. IUPAC NOMENCLATURE OF SPIRO COMPOUNDS

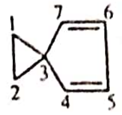
A spiro compound is named by prefixing the word "**spiro**" to the anme of parent hydrocarbon. The parent hydrocarbon is chosen by counting the total number of carbon atoms in both the rings. The numbers in square brackets show the number of carbon atoms on each side of the common carbon between the two rings. The numbering begins from the ring atom *next to the spiro atom, and proceeding first around* the **smaller** *ring and then to the spiro atom and finally around the large ring.* The **number** within the **brackets** are arranged in the **increasing order** of their size. For example,



Spiro [2·4] heptane

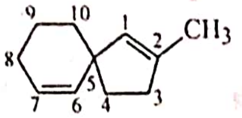


Spiro [2·5]octance

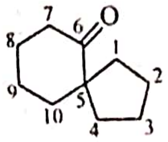


Spiro [2·4] hepta-4,6-diene

Spiro [2·2] pentane



2-Methyl spiro [4·5] deca-1,6-diene



Spiro [4·5] decan-6-one

The nomenclature of **aromatic, polynuclear** and **heterocyclic** compounds will be discussed in concerned chapters.

5.5. PITFALLS TO BE AVOIDED IN IUPAC NAMES

The use of common prefixes like n-, iso-, sec-, tert-, neo-, etc., are to be avoided in IUPAC names as far as possible. For example,

(*i*) $CH_2CH_2CH_2CH_2CH_3$ is named as **Pentane** and not as *n*-pentane.

(*ii*) $CH_3CH(CH_3)CH_2CH_3$ is named as **2-Methylbutane** and not as *isopentane*.

(*iii*) $CH_3CH(C_2H_5)OH$ is named as **2-Butanol** and not as *sec*- butanol.

(*iv*) $CH_3C(CH_3)_2OH$ is named as **2-Methyl-2-propanol** and not as *tert*-butanol.

5.6. PROCEDURE FOR WRITING THE STRUCTURE OF A COMPOUND WITH A GIVEN IUPAC NAME

The steps involved in this procedure are as follows :

(*i*) *Locate the root word, write the principal chain* (straight in the case of open-chain or acyclic compounds and closed in case the root word carries the prefix *cyclo*) *corresponding to the root word and number it from one end* (see also step (*iii*) below for numbering the chain of a compound with a chain-terminating functional group).

(*ii*) *Locate the primary suffix* (*-ane*, *-ene* or *-yne*), *and fill the multiple carbon-carbon bonds*, i *present, at the proper place(s) in the parent chain.*

15

AROMATICITY, ORIENTATION AND CONCEPT OF NUCLEOPHILIC SUBSTITUTION

15.0. INTRODUCTION

Benzene (C_6H_6), the simplest aromatic hydrocarbon, occupies the key position in the study of the chemistry of **aromatic** compounds. In fact, aromatic hydrocarbons containing **benzene** rings or **condensed** system of benzene rings (*e.g.*, naphthalene, anthracene, phenanthrene etc.) are known as **benzenoid** hydrocarbons due to their structural similarity and aromatic properties. There is yet another series of compounds, which exhibit aromatic properties but lack benzene like structures are known as **non benzenoid aromatic** compounds (*e.g.*, azulene, cyclopropenyl cation, heterocyclic compounds, etc). The compounds, which neither possess **benzenoid** structure nor show aromatic properties (aromaticity) are called **anti aromatic** or **non aromatic compounds**.

15.1. AROMATIC CHARACTER (Aromaticity)

Benzene, a representative of the class possesses unique characteristics called aromatic characters. These are :

1. **Comparatively resistant to undergo addition reactions.** Its molecular formula (C_6H_6), suggests a **high degree** of **unsaturation** but it does not respond addition reactions with HBr, alkaline halogens, decolorisation of Br_2-water and Baeyers test, which readily add to alkene double bond. However, benzene does react additively with chlorine but only under conditions necessary for **free radical addition**. Catalytic hydrogenation also occurs but **only** at high temperature and pressure.

2. **High resonance energy**. Its heat of hydrogenation (observed) =208·3 **kJ mol^{-1}** is rather low, compared with that calculated for 1, 3, 5,-cyclohexatriene (358·8 kJ mol^{-1}). This difference between calculated and observed value (358·8-208·3 = **150·5 kJ mol^{-1}**) is known as resonance energy that gives considerable **stability** to benzene.

3. Its heat of combustion 3301·3 kJ mol^{-1} is low as compared to that calculated for cyclohexatriene (3451·8 kJ mol $^{-1}$) by 150·5 kJ mol^{-1}. Hence, there is considerable **stability** of benzene. This is another way of calculating **resonance** energy.

4. It is a *flat cyclic* compound containing a *conjugated* **system** of double bonds with **planar** geometry that alone permits a full **π-overlap** (due to *sp*^{2} hybrid carbons).

5. It undergoes **mainly electrophilic substitution** reactions like **nitration, sulphonation, halogenation**

and **Friedel-crafts** reaction, etc. and *rarely* nucleophilic substitution reactions. These reactions are not given by corresponding open chain *polyenes*.

6. –OH substituted aromatic compounds (like phenols) are appreciably more **acidic** than alcohols. Amino substituted aromatic ring (like aniline) is considerably **weaker base** than aliphatic amine.

Compounds containing one or more benzene rings also possess these features. All these benzene like compounds are called **benzenoid aromatic compounds**. The quality, which imparts **special stability** unique to these compouds is known as **aromatic character or aromaticity**.

It will be seen in due course that the presence of a benzene ring alone is not an essential condition for a compound to show aromatic character. In fact, there are several compounds, which have little resemblance to benzene and yet show the typical aromatic character. Such aromatic compounds are known as **non-benzenoid aromatic compounds** to distinguish from benzenoids.

15.2. HÜCKEL THEORY OF AROMATICITY

The ***latest*** and highly accepted theory of **aromaticity** is given by **Hückel**. Its main postulates are :

1. If the number of π-electrons in a cyclic system is equal to $(4n + 2)$, where $n = 0, 1, 2, 3$, etc. The compound is said to be **aromatic**.

2. This rule is applied to ring carbons containing planar cyclic system in which each carbon is capable of being sp^2 hybridised to ***ensure*** **maximum overlapping** of p-orbitals for extended π-bonding. It is applicable to extended unsaturated **heterocyclics and fused ring** compounds also.

3. An aromatic compound must contain cyclic clouds of delocalised π-electrons above and below the plane of the molecule.

4. All atoms participating in π-bonding must be situated in the same plane. The system may also be an **ion** (cation or anion).

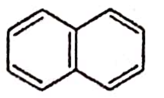
5. The number of π-electrons that fulfill Hückel's rule are **2, 6, 10, 14, 18,** etc, when $n = 0, 1, 2, 3, 4$, etc. These are known as **Hückel numbers.**

6. Cyclic compounds with $(4n)$ π electrons would be even **less stable than their open-chain analogues** and such cyclic compounds are called **anti-aromatic compounds.**

15.2.1. BENZENOID AROMATIC COMPOUNDS

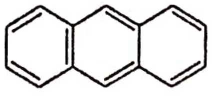
1. Benzene, which is a *planar conjugated monocyclic* compound with a π cloud of six electrons, obeys the Hückel $(4n + 2)$ rule (6 is a Hückel number, when n is equal to 1). The Hückel number **6** is the most common and these six π electrons are known as **aromatic sextet**. Thus, benzene should be, and actually is, a typical aromatic compound.

2. Polycyclic compounds*. Strictly, the Hückel $(4n+2)$ rule is applicable to monocyclic systems only. However, polycyclic conjugated systems like naphthalene (I), anthracene (II) and phenanthrene (III) are the typical **benzenoid aromatics**, the number of π electrons in each case corresponding to Hückel numbers **10** or **14** ($n = 2$ or 3). These also give all aromatic properties.



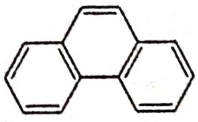
I

Naphthalene
(10π electrons)



II

Anthracene
(14π electrons)



III

Phenanthrene
(14π electrons)

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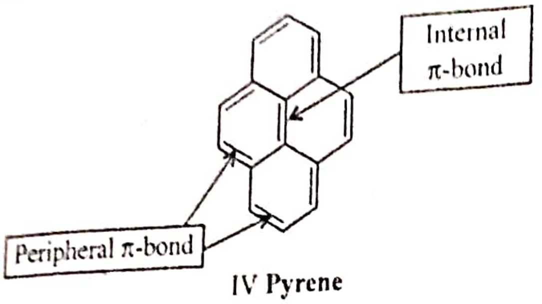
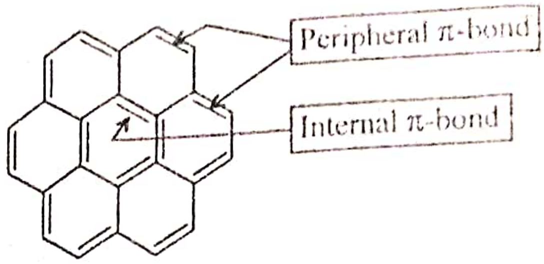
* For isolated polynuclear compounds like diphenyl, triphenyl, etc. individual ring is condidered under $(4n + 2)$ rule for aromaticity. Hence diphenyl, diphenyl methane, etc. are also aromatic.

3. Pyrene IV and coronene V with 16 and 24 π electrons respectively do not obey Hückel rule and it may be expected not to show aromatic character. However, these are typical **benzenoid aromatic** compound as shown by their experimental data. A closer examination of the distribution of π electrons in pyrene and coronene shows that they contain **14** and **18** ***peripheral π electrons*** ($n = 3$ and 4) respectively. Therefore it has been suggested that in such polycyclic systems, the Hückel ($4n + 2$) rule should be applied to peripheral (conjugated) π-electrons only.



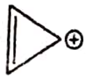
IV Pyrene
(16 π-electron)
14-Peripheral π-electrons
(Behave like **aromatic** compounds)



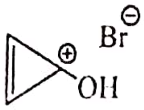
V Coronene
(24 π-electrons)
18-Peripheral π-electrons
(Behave like **aromatic** compounds)

15.2.2. NON-BENZENOIDS AROMATIC COMPOUNDS

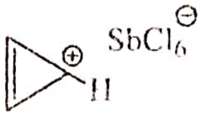
1. Cyclopropenyl cation (I). This cation is a closed-shell of ($4n + 2$) π electrons ($n = 0$). Therefore, it should be a ***stable*** aromatic system. Actually, several ***stable*** cyclopropenium salts have been prepared. For example,



I
Cyclopropenyl cation
(2π-electrons)
(**Three** resonating structures)



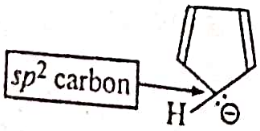
Hydroxycyclopropenyl bromide
(***stable***)
(**Three** resonating structures)



Cyclopropenyl hexachloroantimonate
(***stable***)
(**Three** resonating structures)

These *stable* **cyclopropenium salts** are obviously **non-benzenoid aromatic compounds**. The NMR spectrum of cyclopropenyl cation **(I)** shows **three** equivalent protons.

2. *Cyclopentadienyl anion (II). This anion has three doubly filled M.Os., so that the anion **(II)** is a cyclic ($4n + 2$) π-electron molecule ($n = 1$). This **non-benzenoid** system should be a ***stable*** aromatic system. Actually, stable ***potassium cyclopentadienide*** and ***dicyclopentadienyl iron*** (ferrocene) have been prepared.



II
Cyclopentadienyl anion
(6π-electrons)
(Five resonating structures)

Potassium cyclopentadienide
(***stable***)

Ferrocene
(***stable***)

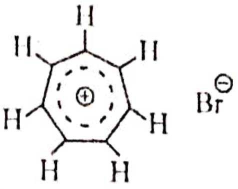
---

* Cyclopropene unlike cyclopropenyl cation is **not aromatic** due to lack of **delocalisation**. Besides following **Huckel rule, high resonance** is also a necessary condition for a compound to be aromatic.

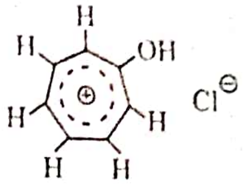
3. **Ferrocene**, an orange solid (m.p. 173°C), has been observed to show aromatic substitution reactions like **Friedel-Crafts** acylation. This is yet another example of a **nonbenzenoid aromatic compound.**

4. **Cycloheptatrienyl cation** (Tropylium ion) (III). This cation, follow a $(4n+2)$ π-electron system should be stable. Stable tropylium salts have actually been prepared, which show **aromatic character**. For M.O. picture see Fig. **15.1**.

III
Cycloheptatrienyl cation
or Tropylium ion (6 π electrons)
(**Seven resonating** structures)

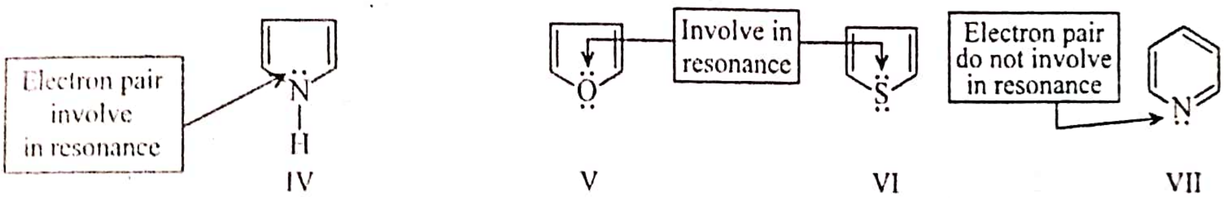


Tropylium bromide
(***stable***)



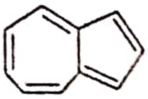
Hydroxytropylium chloride
(***stable***)

5. **Heterocyclic compounds.** *Pyrrole* (IV), *furan* (V), *thiophene* (VI), and *pyridine* (VII) are aromatic because they obey **Hückel Rule** and provide an aromatic sextet in a planar cyclic system. One **extra electron pair** on **hetro atom** in **five** membered hetrocyclics is also considered to act as aromatic sextet to fulfil Hückel rule.



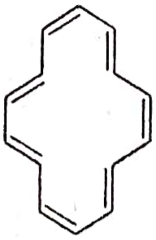
IV Pyrrole (6π-electrons) V Furan (6π-electrons) VI Thiophene (6π-electrons) VII Pyridine (6π-electrons)

6. **Azulene (VIII)** with 10 π electrons should be a **non-benzenoid aromatic compound** because it conforms to the Hückel rule ($n = 2$). Actually, azulene is an intense blue ***stable*** solid (m.p. 99°C) undergoes typical ***electrophilic substitution*** reactions like other aromatic compounds.

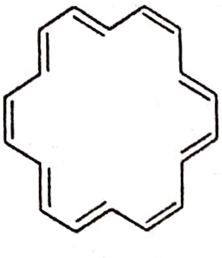


(VIII)
Azulene (10π electrons)

7. **Annulenes**. *Monocyclic conjugated polyenes containing ten* or more carbon atoms in the ring are called* **annulenes.** They are generally named by prefixing the number of carbon atoms placed in square brackets. [14] and [18]-Annulenes, obey the **Hückel's** $(4n + 2)$ rule, and they should, and actually do, show **aromatic** character.



[14] Annulene



[18] Annulene

Annulenes with rather large number (≥ 30) of carbons are generally non-aromatic.

15.2.3. ANTI-AROMATIC AND NON AROMATIC COMPOUNDS

1. **Cyclo-octatetraene** (I) is a bright yellow, non-benzenoid *compound* with alternate single and double bonds in a regular octagon. Such $4n$ π-electron molecules do not possess a closed shell planar configuration in the ground state. Such molecules, therefore, should, and actually do, lack *aromaticity*. Cyclo-octatetraene is, in fact, an *unstable* compound showing a high order of olefinic

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*The term 'annulene' is not generally used for monocyclics containing *fewer* carbons.

reactivity. Such $4n$ π-electron molecules are actually **less stable than their acyclic analogues**, and are known as **anti-aromatic compounds.**

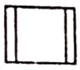
I
Cyclooctatetraene
(8π electrons)

or

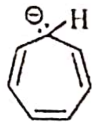
Cyclooctatetraene
(Tub shape)

2. By similar reasoning, cyclic systems/compounds such as *cyclopropenyl anion* II, *cyclobutadiene* III, *cycloheptatrienyl anion* IV and *cyclopentadienyl cation* V should be, and actually are, **anti-aromatic compounds.**

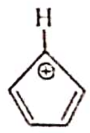
II
Cyclopropenyl anion
(4π-electrons)



III
Cyclobutadiene
(4π-electrons)

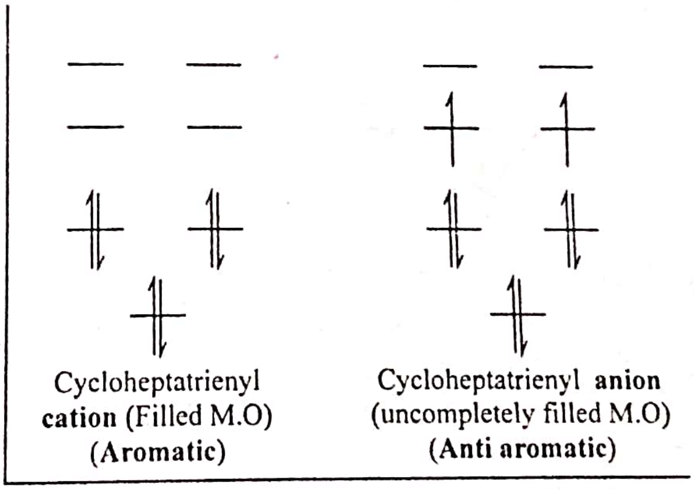


IV
Cycloheptatrienyl
anion (8π-electrons)



V
Cyclopentadienyl cation
(4π-electrons)

The cycloheptatrienyl anion IV has seven equivalent resonating structures and expected to have a well distributed negative charge. But it has an **incomplete molecular orbital shell** with eight π electrons, and this property conveys **antiaromatic** character. Whereas its cation with six π-electrons with complete molecular orbital shell is aromatic (see fig **15.1**). This is an another way to look at the **aromatic** and **antiaromatic** character of the cyclic organic compounds.

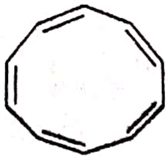


Cycloheptatrienyl **cation** (Filled M.O) **(Aromatic)**

Cycloheptatrienyl **anion** (uncompletely filled M.O) **(Anti aromatic)**

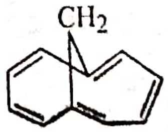
Fig. 15.1. Molecular orbital energy levels for cycloheptatrienyl cation and anion.

3. **Cyclodecapentaene** (VI) containing 10 π-electrons has planar all-*cis* structure with highly strained bond angles. The alternative structure with two-*trans* double bonds VII cannot achieve planarity due to the interaction between two interior hydrogens. As a result, cyclodecapentaene does not give aromatic character. It is therefore, **non aromatic.**



VI
all *cis*-Cyclodecapentaene
(Non aromatic)

VII
(Z, Z, E, Z, E)
Cyclodecapentaene



VIII
Bicyclo [4, 4, 1]
undeca-1, 3, 5, 7, 9 pentaene
(Aromatic)

It we replace two interior hydrogens of structure VII by a bridging methylene group, the resulting hydrocarbon VIII cannot have completely coplanar π-system but sufficient ovelap occurs to give significant aromatic character.

To sum up, ***a cyclic compound would be aromatic if***

(i) it has a planar or nearly planar structure,

(ii) it has (4n+2) π-electrons.

(iii) it shows unusual stability as shown by large **resonance** *or* **delocalisation** *energy.*

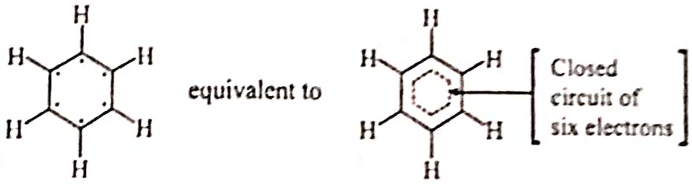
(iv) it undergoes ***electrophilic substitution*** *rather than addition reactions.*

(v) it may or may not contain a benzene ring.

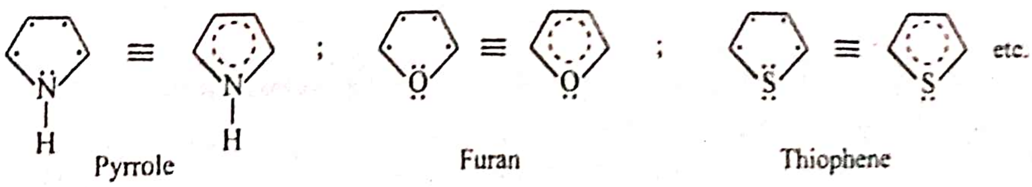
These terms have been distinguished from one another by comparing the π electron energy of a particular cyclic system with corresponding acyclic (or open-chain) system. Cyclic compounds arise by removing a hydrogen from each terminal carbon of a chain and then joining the terminal carbons. *When the π electron energy of a cyclic system (say, benzene) is less than that of the corresponding acyclic (say, 1,3,5-hexatriene) system, the cyclic system is known as* **aromatic**. *When the cyclic system has the π electron energy equal to that of the corresponding acyclic system, the cyclic system is* **non-aromatic**. *When the π electron energy of a cyclic system (say, cyclobutadiene) is more than that of the corresponding acyclic system (say, 1,3-butadiene) the cyclic system is* **anti-aromatic.**

15.3. AROMATIC SEXTET THEORY

This theory was proposed by Robinson (1925) to explain aromaticity in benzene (C_6H_6). According to this theory, there are six electrons more than required to link together the six carbon and six hydrogen atoms of the benzene ring. One remaining electron of p_z orbital on each carbon form a **closed circuit** and this closed circuit of six electrons provides greater stability and aromatic character to benzene.



This closed circuit of six electrons which makes the molecule aromatic is known as **aromatic sextet**. Such closed circuit of six electrons, is also possible in heterocyclic compounds like pyrrole, furan, thiophene and pyridine and hence they are **aromatic**. The *hetero* atom of five membered heterocycles contribute two electrons to **aromatic sextet** as shown below.



This closed circuit of six electrons corresponds to Hückel's $(4n + 2)$ rule, where $n = 1$.

15.4. RESONANCE THEORY / VALENCE BOND THEORY

This theory has already been explained in detail in earlier chapter under section **14.8**, page 301.

15.5. MOLECULAR ORBITAL THEORY

The detailed aspect of this part has already been discussed earlier under section **14.11** and 301..