

HETEROCYCLIC COMPOUNDS

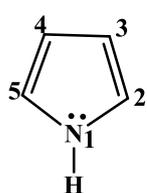
A cyclic compound (ring compound) is a term for compound in the field of Chemistry in which one or more series of atoms in the compound is connected to form a ring.

Cyclic compounds have a ring structure hence called cyclic. If carbon is present in the ring, it is called homocyclic compound, But if one or more of the carbon atoms is replaced by any heteroatoms as S, N, O etc. are called heterocyclic compounds.

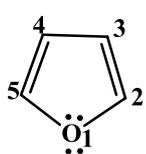
Note- Another heteroatoms such as B, P or Si also form heterocyclic compounds.

Homo= same

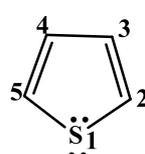
Hetero= different



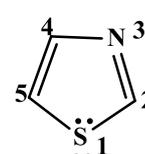
Pyrrole
(Azole)



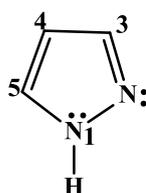
Furan
(Oxole)



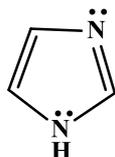
Thiophene
(Thiole)



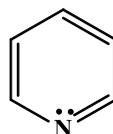
1,3- Thiazole
(Thiazole)



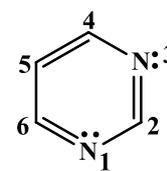
Pyrazole (1,2-diazole)



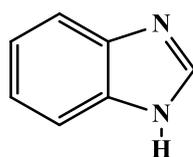
Imidazole (1,3-diazole)



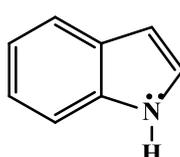
Pyridine



Pyrimidine
(1,3-diazine)



Benzimidazole



Indole

Classification:

Depending upon their structures, heterocyclic compounds may be of three types:

A. Five-membered heterocyclics :

Compounds with five-membered ring and one or more heteroatoms in them are referred to as five membered heterocyclic compounds.

Eg.- Pyrrole, Furan, Thiophene, Thiazole, Imidazole, Pyrazole.

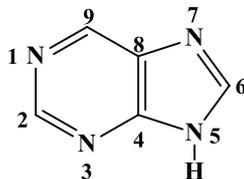
B. Six- membered heterocyclics :

Compounds with six-membered ring and one or more heteroatoms in them are referred to as six membered heterocyclic compounds.

Eg.- Pyridine and Pyrimidine.

C. Condensed (fused) heterocyclics :

They consist of two or more rings fused together. The fused rings may be partly carbocyclic or partly heterocyclic (Indole, Benzimidazole) or completely heterocyclic (Purine).

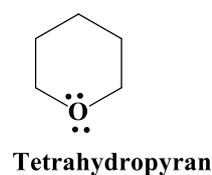
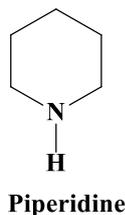
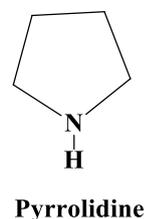
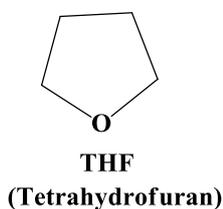


Purine (Pyridine + Imidazole)

Depending on their properties, heterocyclics may be of two types:

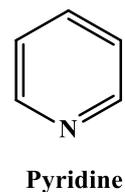
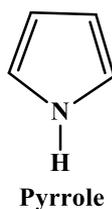
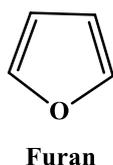
A. Heteroparaffins or non-aromatic heterocyclics:

They resemble paraffins in their properties and are not aromatic in nature.



B. Heterocyclics or aromatic heterocyclics:

They resemble aromatic compounds in their properties and are aromatic in nature.



Nomenclature:

- The systematic names for monocyclic compounds are given by using prefix for the nature of heteroatom present and dropping 'a' whenever necessary.
Eg.- Oxa (for Oxygen), thia (Sulphur), aza (nitrogen) etc. If two or more similar heteroatoms are present, the prefix di, tri etc. are used.
Eg.- Triaza, Trioxa etc. If heteroatoms are different, the order starts from heteroatom of the highest group in the Periodic table and as low as an atomic number, when in same group. Eg.- O, S, N, P (O then N).
- The size of the monoheterocyclics is indicated by suffix- ole (5-membered), -ine (6-membered) etc.

3. If monoheterocyclic numbering is given in such a way that heteroatom gets the lowest number and it proceeds anticlockwise around the ring.
4. When heteroatoms are different, the numbering starts according to point no.-1 and proceeds round the ring in order of precedence or priority.

Seven- and Larger-Membered Heterocyclic Compounds (Containing Two or More Heteroatoms – M.Sc Level)

Introduction

Seven- and larger-membered heterocyclic compounds containing two or more heteroatoms are generally non-aromatic, flexible, and less stable than five- and six-membered rings. They play important roles in medicinal and coordination chemistry.

Seven-Membered Heterocycles

Diazepines

Structure: Seven-membered ring with two nitrogen atoms.

Synthesis: Condensation of diamines with diketones; ring expansion reactions.

Reactions: N-alkylation, hydrolysis, reduction to diazepam.

Oxazepines

Structure: Seven-membered ring containing oxygen and nitrogen.

Synthesis: Cyclization of o-aminophenols with carbonyl compounds.

Reactions: N-alkylation, reduction, ring opening reactions.

Thiazepines

Structure: Seven-membered ring with sulfur and nitrogen.

Synthesis: Cyclization of o-aminothiophenols.

Reactions: Oxidation at sulfur, N-alkylation, ring cleavage.

Eight- and Larger-Membered Heterocycles

Diazocines

Structure: Eight-membered ring with two nitrogen atoms.

Synthesis: High-dilution cyclization and ring expansion methods.

Reactions: Protonation, N-substitution, ring opening reactions.

Macrocyclic Heterocycles

Examples: Porphyrins, crown ethers, cryptands.

Synthesis: Template-directed and high-dilution methods.

Reactions: Metal ion coordination, oxidation, substitution reactions.

Conclusion

Seven- and larger-membered heterocycles exhibit unique reactivity due to reduced aromaticity and increased flexibility, making them significant in advanced organic and medicinal chemistry.