Tishk International University

Faculty of Dentistry

Department of Basic Science

Organic Chemistry

Aromatic Compounds

4th lecture

1st grade

➢ Aliphatic compounds:

Aliphatic compounds are ***open-chain*** *(straight or branched)* compounds or cyclic compounds. The families we have studied so far *alkanes*, *alkenes*, *alkynes*, and their *cyclic* compounds are all members of the ***aliphatic class***.

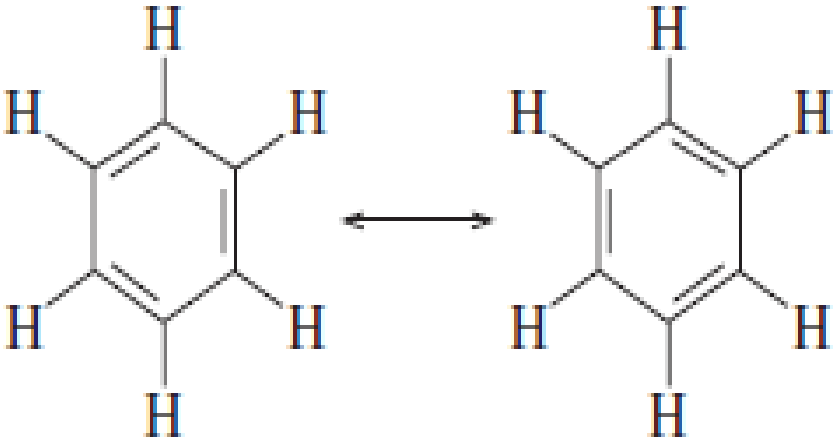
Aliphatic compounds can have a mix of ***(single, double or triple)*** bonds between them. This means that they can be **saturated** or **unsaturated.**

➢ Aromatic compounds:

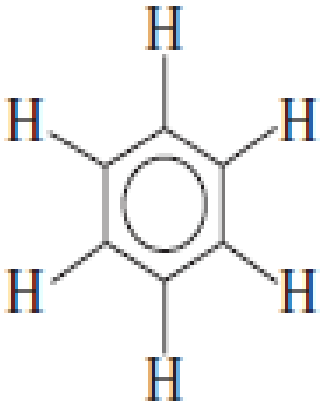
Are compounds that consist of ***one*** or ***more*** rings that contain alternating single and double bonds in its chemical structure ***(i.e. conjugated double bond)***.

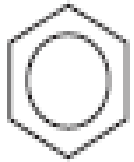
In 1825, Michael Faraday isolated a hydrocarbon called ***benzene***, which had the molecular formula **[C_6H_6]**. A molecule of **benzene** consists of a ring of six carbon atoms with one hydrogen atom attached to each carbon.

Many compounds that contain benzene ring have ***fragrant odors***, that's why family of benzene compounds known as **aromatic compounds**.



Structures for benzene





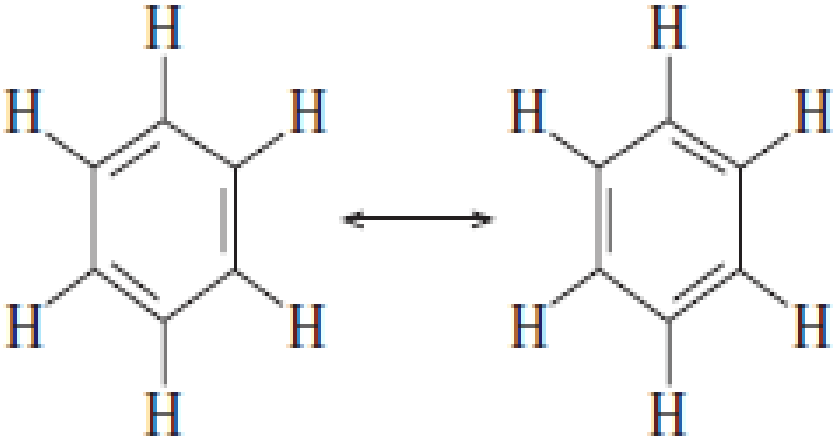
Skeletal formula for benzene ring

➢ Characteristics of aromatic compounds:

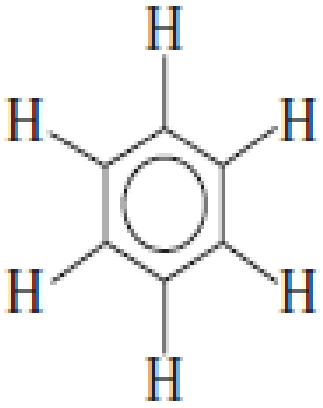
An aromatic compound contains a set of covalently bound atoms with specific characteristics:

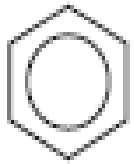
1. A delocalized conjugated π system :

Delocalized electrons are electrons that are not ***attached*** on a ***fixed*** atom. In the ring of an aromatic compound, ***electrons*** are ***delocalized***, so they are spread out over the ring. In benzene, the two structures show that the double bonds can be moved about the ring because the electrons are ***delocalized*** within the ring. *That is why alternating double bonds in the ring can also be illustrated as a circle.*



Structures for benzene





Skeletal formula for benzene ring

2. ***Coplanar structure:*** all the contributing (participated) atoms are in the same plane.

3. Atoms arranged in one or more rings.

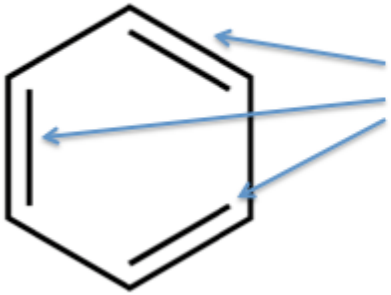
4. Obeys ***huckel's*** rule .

➢ Huckel's Rule:

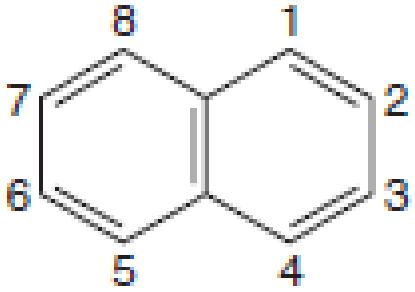
We saw that there are double bonds in the ring that is present in the chemical structure of aromatic compounds. These double bonds contain electrons called ***'pi electrons'*** The number of *(pi)* electrons is very important in determining if the compound ***obeys*** Huckel's Rule or not.

- **Huckel's Rule** states that an aromatic compound must have a certain number of *(pi)* electrons. The number of *pi* electrons must be equal to **(4n+2)**, where ***n*** is equal to zero or any positive integer (***n* = 0, 1, 2,3,…etc.**).

Benzene



3 double bonds = 6 pi electrons



Naphthalene

$C_{10}H_8$

Huckel's rule:

4n + 2 = pi electrons

4n + 2 = 6

4n = 4

n = 1

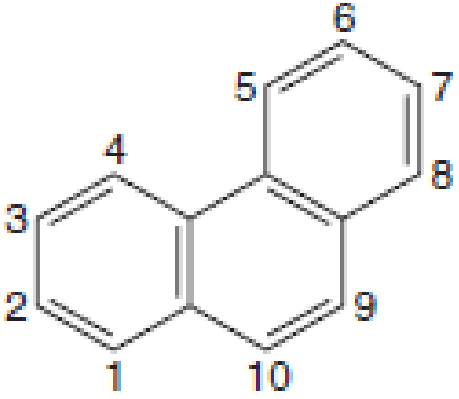
Huckel's rule:

4n + 2 = pi electrons

4n + 2 = 10

4n = 8

n = 2



Phenanthrene
$C_{14}H_{10}$

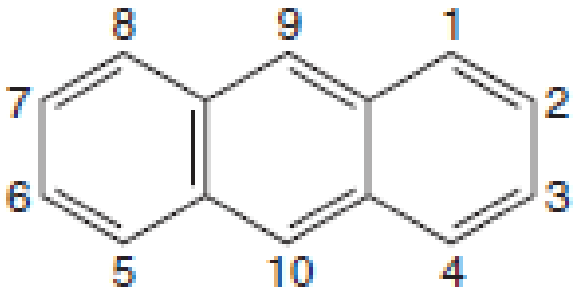
Huckel's rule:

4n + 2 = pi electrons

4n + 2 = 14

4n = 12

n = 3



Anthracene
$C_{14}H_{10}$

Huckel's rule:

4n + 2 = pi electrons

4n + 2 = 14

4n = 12

n = 3

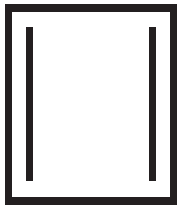
➢ Antiaromatic compounds:

1. The molecule must be cyclic.

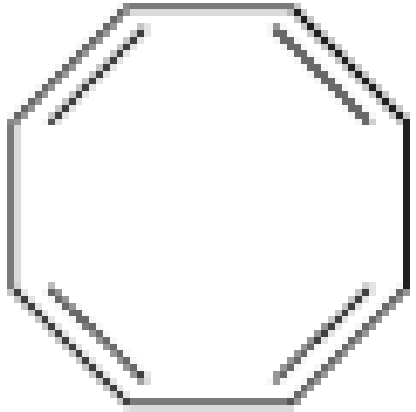
2. The molecule must be planar.

3. The molecule must have a complete conjugated π-electron system within the ring.

4. The molecule must have $4n$ π-electrons where n is any integer number.



Cyclobutadiene



4n = pi electrons

4n = 4

n = 1

4n = pi electrons

4n = 8

n = 2

➢ Carbon-carbon bond lengths in benzene:

All carbon-carbon bonds in benzene are equal and they are intermediate length between carbon-carbon single bond and carbon-carbon double bond. Carbon-carbon double bonds in a wide variety of compounds are found to be about ***1.34 A^0*** long and ***1.53 A^0*** for carbon-carbon single bond.

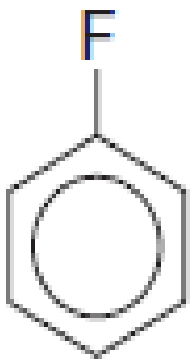
Studies show that the six carbon-carbon bonds in benzene are equal and have a length of ***1.39 A^0***, and are thus intermediate between single and double bonds.

Nomenclature of Benzene Derivatives

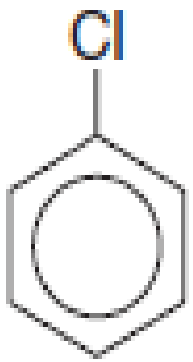
- **Monosubstituted:**

Two systems are used in naming Monosubstituted benzenes.

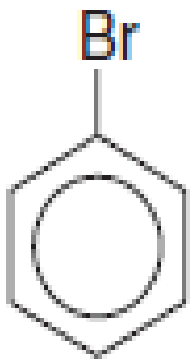
In many simple compounds, *benzene* is the parent name and the substituent is simply indicated by a ***prefix***. For example;



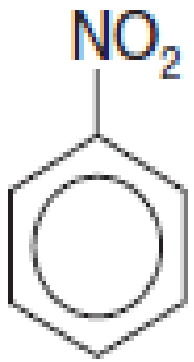
Fluorobenzene



Chlorobenzene



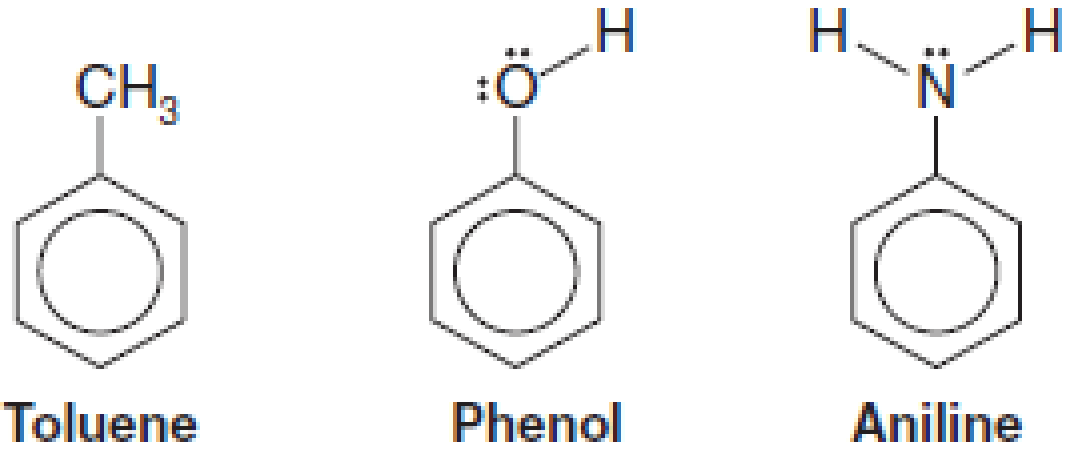
Bromobenzene



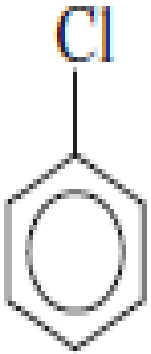
Nitrobenzene

For other simple and common compounds, the substituent and the benzene ring taken together may form a commonly accepted parent name.

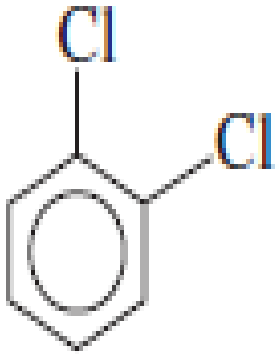
Methylbenzene is usually called ***toluene***, *hydroxybenzene* is almost always called ***phenol***, and *aminobenzene* is almost always called ***aniline***:



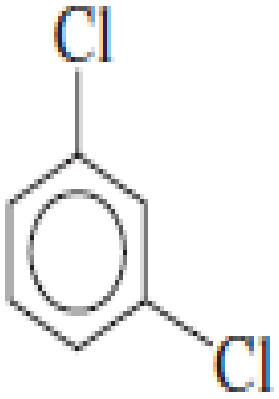
When benzene has only *one* substituent, the benzene ring is not numbered. When there are *two or more substituents*, the benzene ring *is numbered to give the lower numbers to the substituents*.



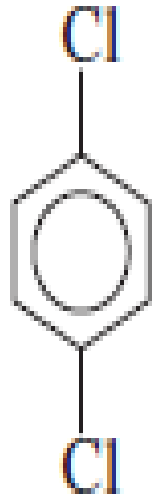
Chlorobenzene



1,2-Dichlorobenzene

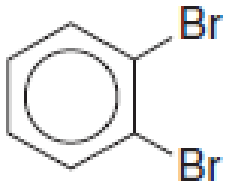


1,3-Dichlorobenzene

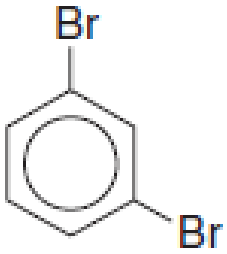


1,4-Dichlorobenzene

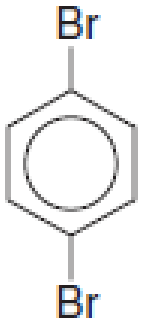
When two substituents are present, their relative positions are indicated by the prefixes ***ortho-***, ***meta-***, and ***para-*** (abbreviated ***o-***, ***m-***, and ***p-***) or by the use of numbers.



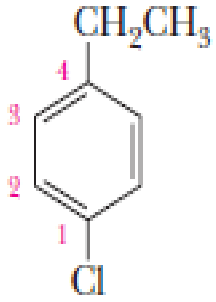
1,2-Dibromobenzene
(*o*-dibromobenzene)
ortho



1,3-Dibromobenzene
(*m*-dibromobenzene)
meta

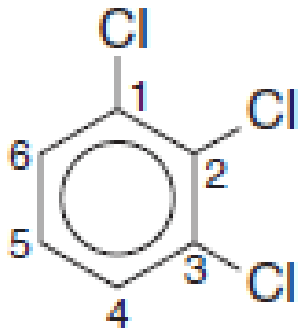


1,4-Dibromobenzene
(*p*-dibromobenzene)
para

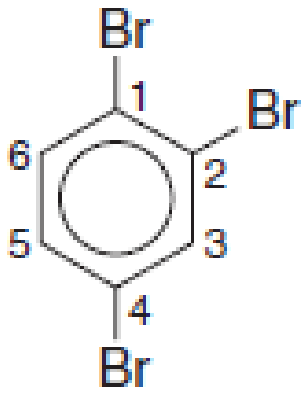


1-Chloro-4-ethylbenzene
(*p*-Chloroethylbenzene)

If ***more than two*** groups are present on the benzene ring, their positions must be indicated by the use of ***numbers*.**



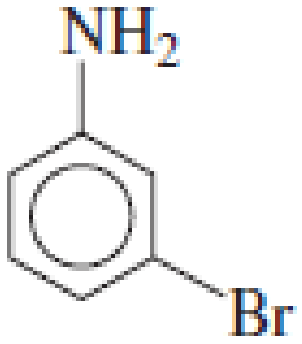
1,2,3-Trichlorobenzene



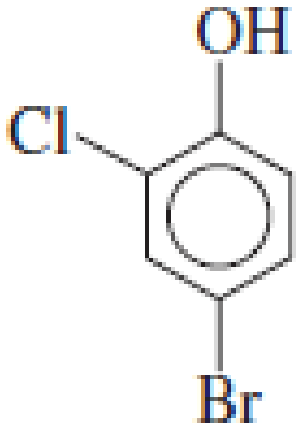
1,2,4-Tribromobenzene
(*not* 1,3,4-tribromobenzene)

The benzene ring is numbered so as to give ***the lowest possible numbers to the substituents***.

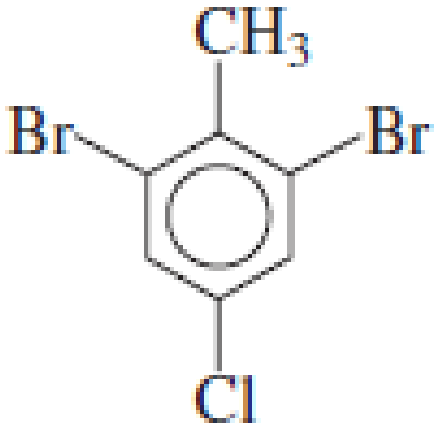
When a common name such as ***toluene, phenol, or aniline*** can be used, the ***carbon*** atom attached to the methyl, hydroxyl, or amine group is numbered as carbon number one. Then the substituents are named alphabetically.



3-Bromoaniline



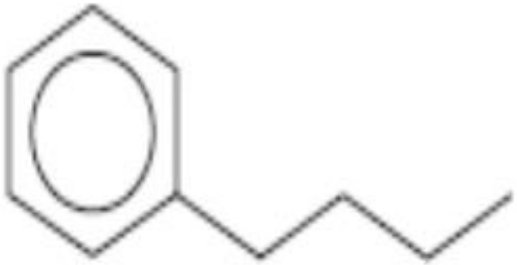
4-Bromo-2-chlorophenol



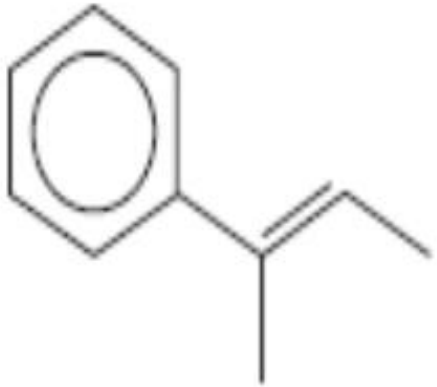
2,6-Dibromo-4-chlorotoluene

When the **C_6H_5-** group is named as a substituent, it is called a **phenyl** group. The phenyl group is often abbreviated as **C_6H_5-** or **Ph-**

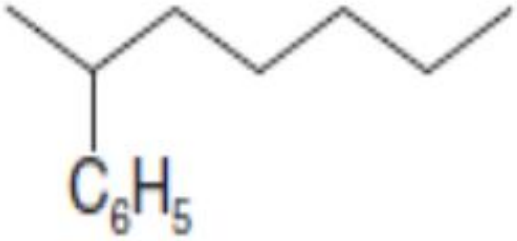
When a hydrocarbon composed of one ***saturated chain*** and one benzene ring is usually named as a derivative of the ***larger structural unit***. However, if the chain is ***unsaturated***, the compound may be named as a ***derivative*** of that ***chain***, regardless of ring size. The following are examples:



Butylbenzene

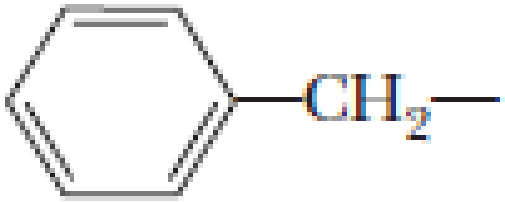


2-Phenyl-2-butene



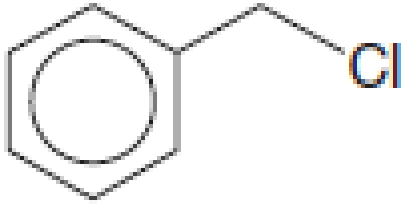
2-Phenylheptane

Benzyl is an alternative name for the ***phenylmethyl*** group. It is sometimes abbreviated Bn.



Benzyl group, Bn–

The benzyl group (the phenylmethyl group)



Benzyl chloride (phenylmethyl chloride or BnCl)

Heterocyclic compounds:

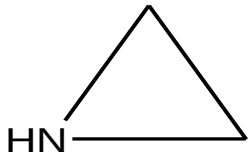
Almost all of the cyclic molecules that we have discussed so far have had rings composed of carbon atoms. However, in many cyclic compounds an element other than carbon is present in the ring. A heterocyclic compound is one that contains a ring made up of *more than one kind of atom which is known as* ***heteroatom*****.**

In most of the cyclic compounds that we have studied the rings are made up only of carbon atoms; such compounds are called ***homocyclic*** compounds. But there are also rings containing, in addition to carbon, other kinds of atoms, most commonly ***nitrogen, oxygen, or sulfur***.

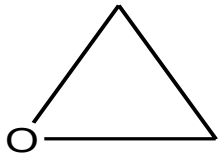
➢ Classification of heterocyclic compounds:

➢ Depending upon the size of heterocyclic ring, they are classified into different types:

1. **Three membered heterocyclic compounds:**

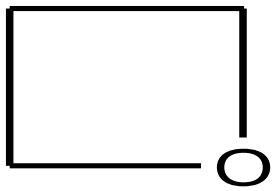


aziridine



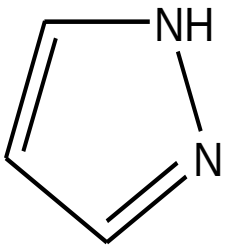
oxirane

2. **Four membered heterocyclic compounds:**

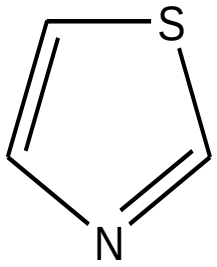


oxetan

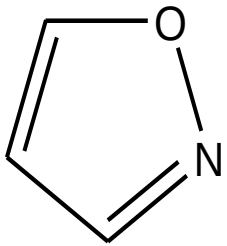
3. Five membered heterocyclic compounds:



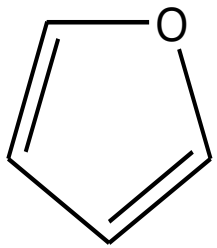
pyrazole



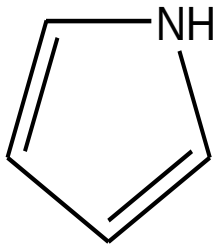
thiazole



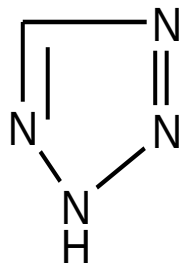
isooxazole



furan

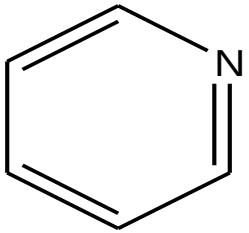


pyrrole

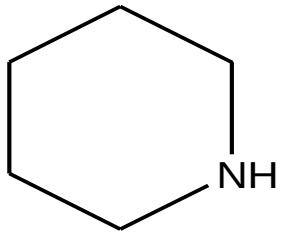


tetrazole

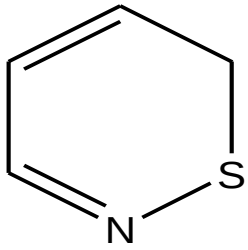
4. Six membered heterocyclic compounds:



Pyridine

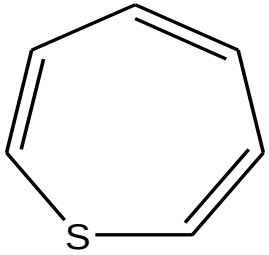


piperidine



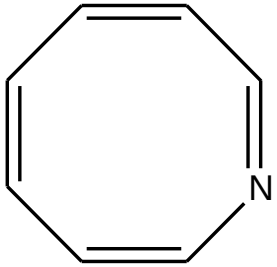
thiazine

5. Seven membered heterocyclic compounds:



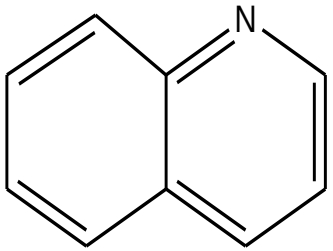
thiepine

6. Eight membered heterocyclic compounds:

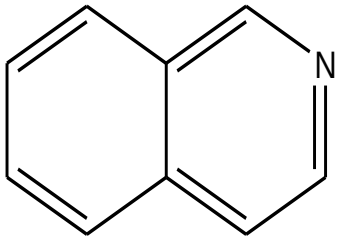


azocine

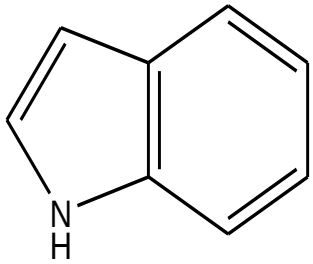
7. Fused heterocyclic compounds:



quinoline



isoquinoline



indole

H.W.: Draw structural formulas for each of the following:

1. *m* - Dinitrobenzene
2. *p* - Bromotoluene
3. Benzyl bromide
4. *p* - Methylphenol

References:

1. Organic chemistry by morrison and boyd.
2. Organic chemistry by solomon and fryhl, 10th Edition, 2011.