Aromaticity and Benzene

Dr. Sadique Akhtar Javed

Dr. Karam Ahmed

Faculty of Pharmacy

Jazan University

Benzene

- All organic compounds have been divided into two broad classes, i.e., aliphatic compounds and aromatic compounds.
- **Aliphatic compounds** are open chain compounds and those cyclic compounds that resemble the open chain compounds. Examples are alkanes, alkenes, alkynes and their cyclic analogues.
- **Aromatic compounds** are benzene and compounds resembles benzene in chemical behavior.

Structure of benzene

Molecular formula, Kekule Structure

- From the elemental composition and molecular weight, benzene was known to have six carbon atoms and six hydrogen atoms and has molecular formula **C_6H_6**.

The question was: how these atoms are arranged?

- In 1865, August Kekule´ proposed the structure of benzene (C_6H_6). According to his proposals, in benzene:

(a) all six carbon atoms are in a ring.

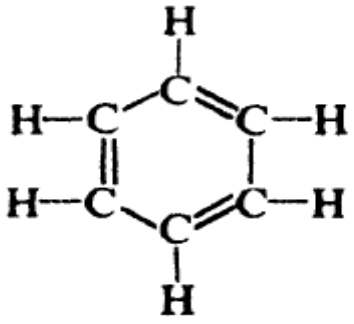
(b) all carbon atoms are bonded to each other by alternating single and double bonds.

(c) one hydrogen atom is attached to each carbon atom.

(d) all hydrogen atoms are equivalent.

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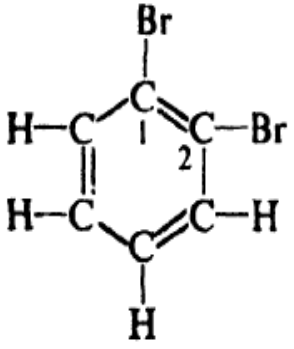
- The Kekule structure of benzene can be represented as:



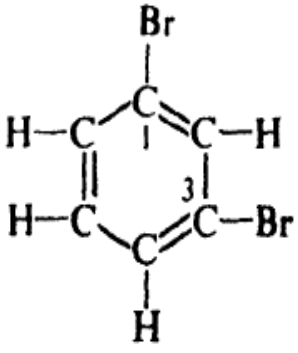
- **Benzene yields only one monosubstitution product, C_6H_5Y:** Only one bromobenzene (C_6H_5Br) is obtained when one hydrogen atom is replaced with bromine. Similarly only one chlorobenzene and only one nitrobenzene has been made.

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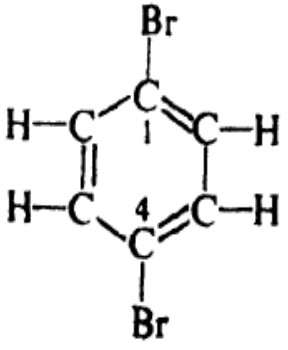
- **Benzene yields three isomeric disubstituted products ($C_6H_4Y_2$ or C_6H_4YZ):** Three and only three dibromobenzene ($C_6H_4Br_2$), three chloronitrobenzens ($C_6H_4ClNO_2$) etc have ever been made.
- The three isomeric dibromo derivatives are 1,2-, 1,3- and 1,4-dibromo compounds as shown:



1,2-Dibromobenzene



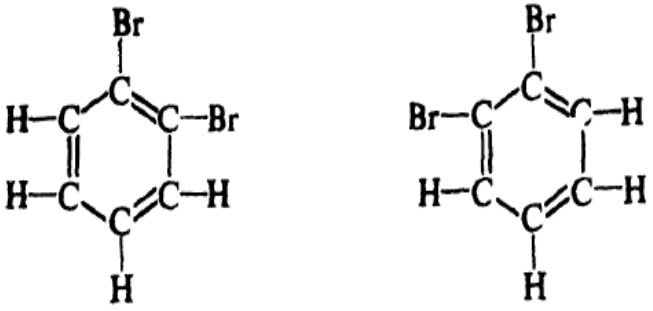
1,3-Dibromobenzene



1,4-Dibromobenzene

Limitations of Kekule´ structure

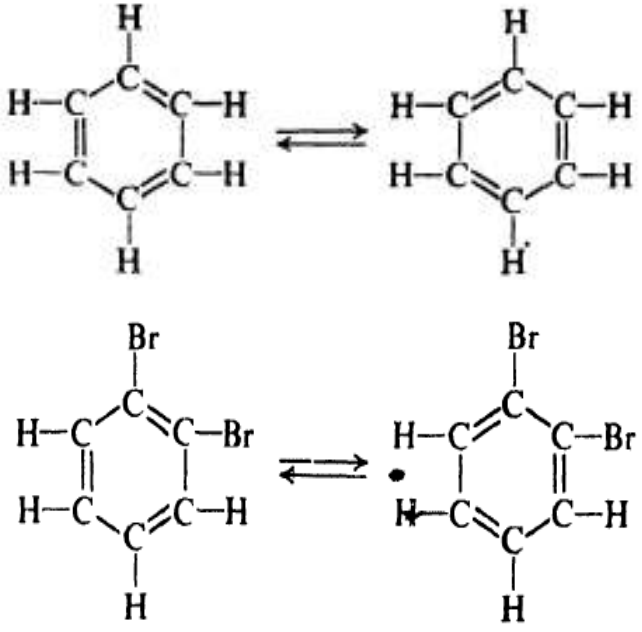
- The Kekule´ structure predicts that there should be two different 1,2-dibromobenzenes.
- Closer examination of the above structure shows, however, that two 1,2-dibromo isomers differing in the positions of bromine relative to the double bonds should be possible.



- In practice, only one 1,2-dibromobenzene has ever been found. Kekule´ proposed that these two forms are in rapid equilibrium and hence could not be separated.

Aromaticity and Benzene

- *Later, this proposal was proved to be incorrect, because no such equilibrium exists!*



- Benzene cannot be represented accurately by either individual Kekule´structure, and does not oscillate back and forth between two.
- The Kekule´structure also cannot explain the stability of benzene.

➢ Stability of Benzene ring. Reactions of Benzene

- Kekule's structure accounts satisfactorily for the facts:

1) Benzene has the molecular formula C_6H_6
2) Benzene yields only one monosubstituted product (C_6H_5Y)
3) Benzene yields three isomeric disubstituted products ($C_6H_4Y_2$ or C_6H_4YZ)

- But there are a number of facts that are still not accounted for this structure, most of these unexplained facts seemed related to **unusual stability of the benzene ring**.

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Bnezene undergoes substitution rather than addition

- Kekule's structure of benzene is one that we would call *"cyclohexatriene."*
- We would expect this cyclohexatriene, like the very similar compounds, cyclohexadiene and cyclohexene, to undergo readily the addition reactions characteristic of alkene structure.
- Actually this is not the case, under conditions that cause an alkene to undergo rapid addition, benzene reacts either not at all or very slowly.

Cyclohexene vs Benzene

Reagent	Cyclohexene gives	Benzene gives
$KMnO_4$ (cold, dilute, aqueous)	Rapid oxidation	No Reaction
Br_2/CCl_4	Rapid addition	No reaction
HI	Rapid addition	No reaction
H_2 + Ni	Rapid hydrogenation at 25°C	Slow hydrogentaion at 100-200°C

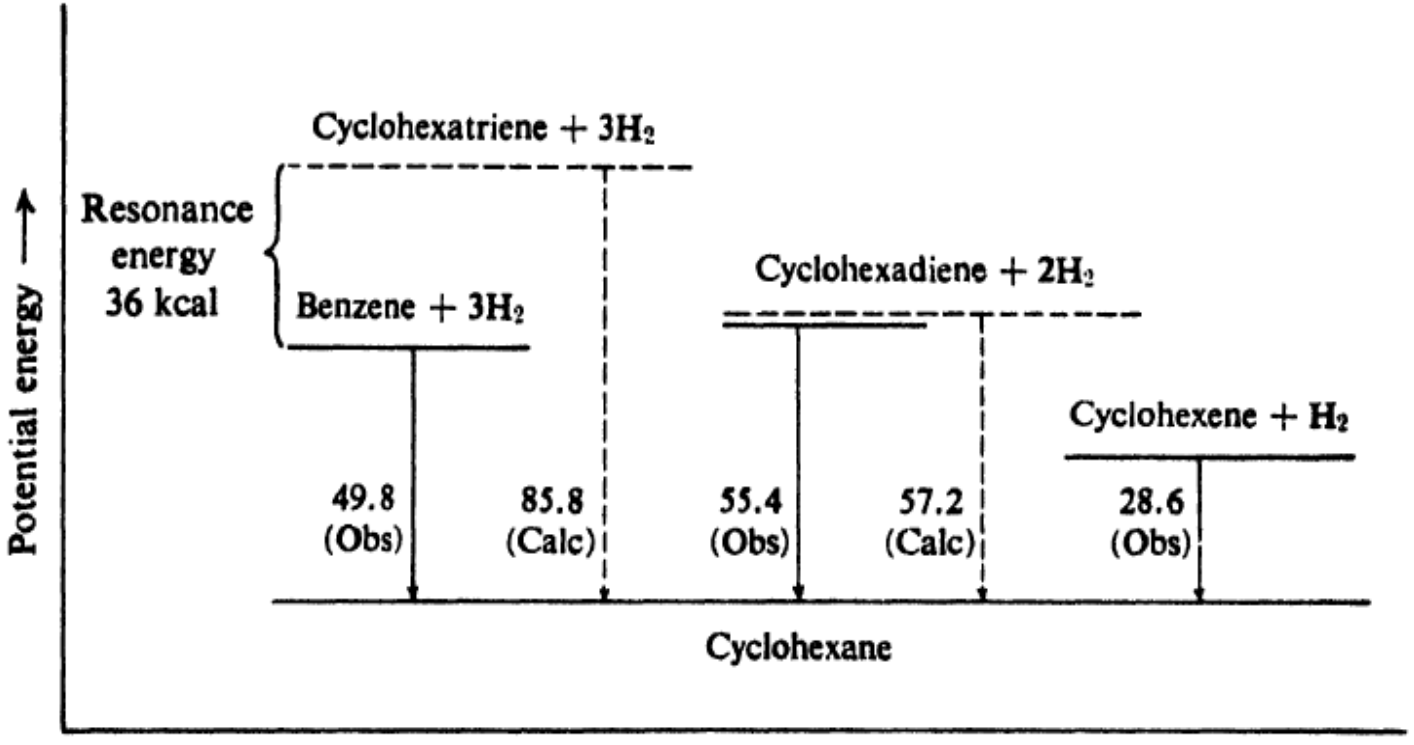
- In place of addition reactions, benzene readily undergoes substitution reactions. Examples, Nitration, sulfonation, halogenation, friedel-craft alkylation, friedel-craft acylation etc.
- Benzene resists addition in which the benzene ring system would be destroyed, whereas it readily undergoes substitution, in which the benzene ring system is preserved.

➢ Stability of benzene. Heat of hydrogenation

- The energy evolved in the hydrogenation of cyclohexene to cyclohexane is 28.6 kcal/mol. Therefore, in the case of cyclohexadiene, where there are two double bonds, the heat of hydrogenation can be calculated as 2 x 28.6 = 57.2 kcal/mol. In practice, the experimental value is quite close to this calculated value, and is 55.4 kcal/mol.
- In this way, if benzene were really a cyclohexatriene as proposed by Kekule´, the calculated evolved heat would be three times than that of cyclohexene, i.e. 3 x 28.6 = 85.8 kcal/mol. *In practice, it was found that the evolved heat for benzene is 49.8 kcal/mol.*

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- This can be represented by the following diagram, in which the height of the horizontal line represents the potential energy content of a molecule. The broken lines represent the expected values based upon three equal steps of 28.6 kcal



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- So benzene evolves 36 kcal less energy than predicted, which means that benzene contains 36 kcal less energy than predicted. In other words, benzene is more stable by 36 kcal than we would have expected cyclohexatriene to be.
- This 36 kcal/mol is known as the **stabilization energy or resonance energy**. This explains the stability of benzene.
- Due to this stabilization energy, benzene does not undergo similar reactions to a cycloalkene.

The resonance explanation of the structure of benzene

- The resonance theory can be applied successfully to explain the structure of benzene.

According to resonance theory:

1) resonance forms are imaginary, not real;
2) resonance structures differ only in the positions of their electrons;
3) different resonance forms do not have to be equivalent;
4) the more resonance structures there are, the more stable the molecule is;
5) whenever it is possible to draw two or more resonance structures of a molecule, none of the structures will be in complete agreement with the compound's chemical and physical properties;

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6) the actual molecule is better represented by a hybrid of these structures;

7) whenever an equivalent resonance structure can be drawn for a molecule, the molecule (or hybrid) is much more stable than any of the resonance structures could be individually if they could exist.

If we consider the Kekule´ structure of benzene, it is evident that the two proposed structures differ only in the positions of the electrons.

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- Therefore, in spite of being two separate molecules in equilibrium, they are indeed two resonance contributors to a picture of the real molecule of benzene.

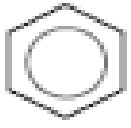


Two structures of benzene as suggested by Kekulé

- If we think of a hybrid of these two structures, then the C-C bonds in benzene are neither single bonds nor double bonds. They should have a bond length between a single (1.47 Å) and a double bond (1.33 Å).

Aromaticity and Benzene

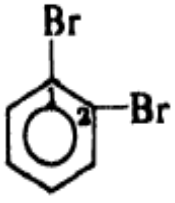
- It has actually been proven that benzene is a planar molecule, and all of its C-C bonds are of equal length (1.39 Å). The bond length (1.39 Å) is indeed in between a single and a double bond!
- Thus, instead of drawing the benzene structure using alternative single and double bonds, a hybrid structure can be drawn.
- The hybrid structure of benzene is represented by inscribing a circle in the hexagon.
- With benzene, the circle represents the six electrons that are delocalized about the six carbon atoms of the benzene ring.



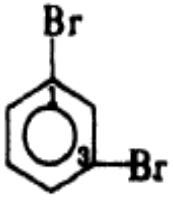
Hybrid structure of benzene

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- The resonance theory accounts for the much greater stability of benzene when compared with the hypothetical 1,3,5-cyclohexatriene.
- It also explains why there is only one 1,2-dibromobenzene rather than two.
- When it is realized that all carbon-carbon bonds in benzene are equivalent, there is no longer any difficulty in accounting for the number of isomeric disubstitution products.
- It is clear that there should be just three, in agreement with experiment:



1,2-Dibromobenzene



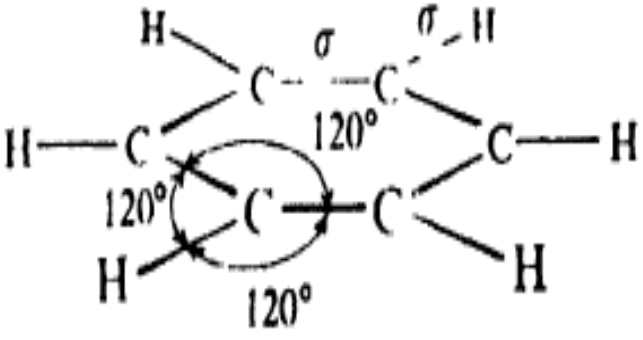
1,3-Dibromobenzene

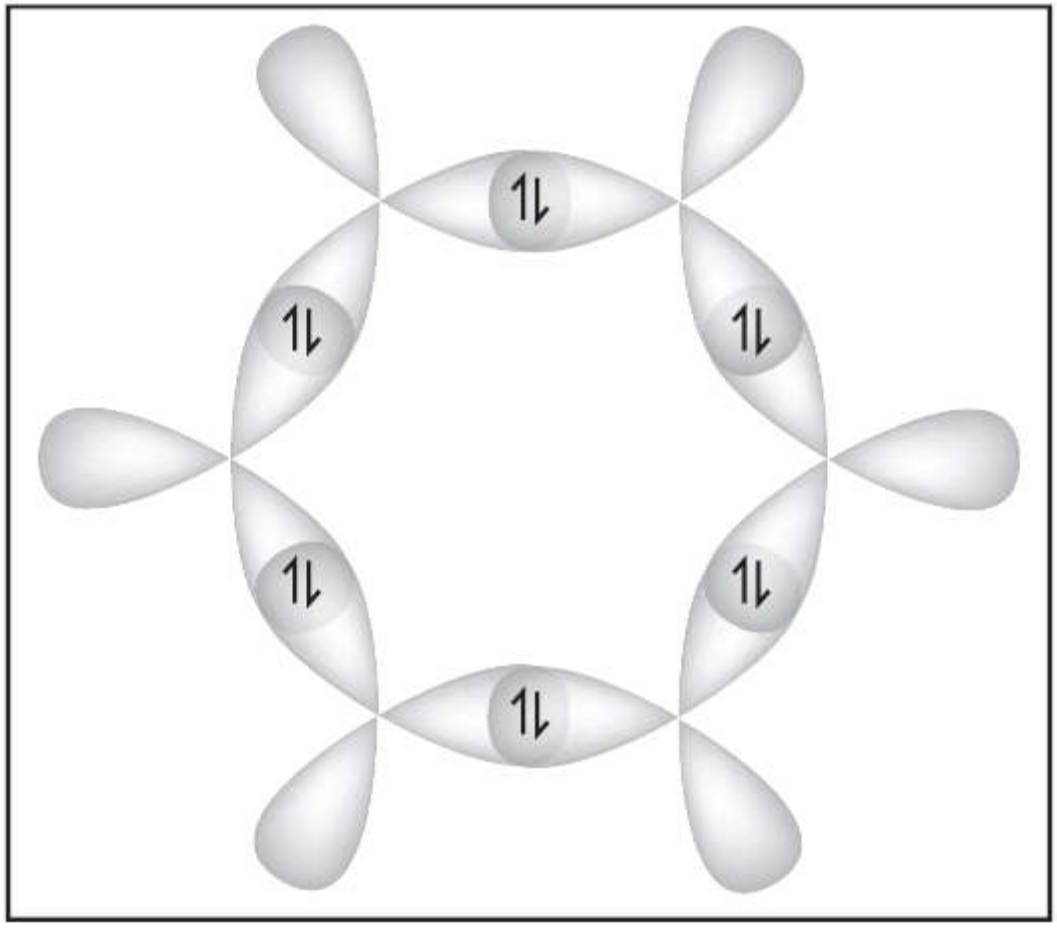


1,4-Dibromobenzene

The molecular orbital explanation of the structure of benzene

- Each carbon in benzene is bonded to three other atoms and it uses sp^2 hybrid orbitals. These orbitals lie in the same plane, that of the carbon nucleus.
- If we arrange the six carbon and six hydrogen of benzene to permit maximum overlap of these orbitals, the following structure will be obtained:



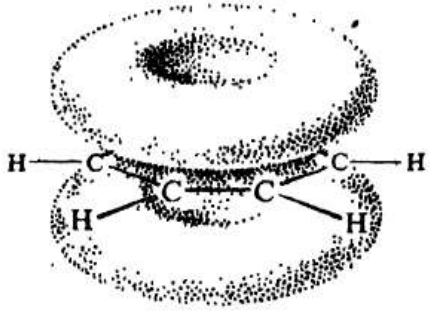


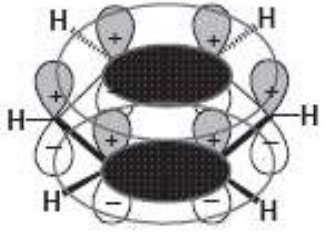
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- Benzene is a ***flat molecule***, with every carbon and every hydrogen lying in the same plane.
- It is a very ***symmetrical molecule*** too, with each carbon atom lying at the angle of a regular hexagon, **every bond angle is 120º** and these bonds are σ bonds.
- The molecule is not yet complete, there are still six electrons to be accounted for.
- In addition to three orbitals already used, each carbon atom has fourth orbital, a *p* orbital.
- As we know, this p orbital consists of two equal lobes, one lying above and the other lying below the plane of the other three orbitals, that is, above and below the plane of the ring, it is occupied by a single electron.

Aromaticity and Benzene

- The *p* orbital of one carbon can overlap the *p* orbital of an adjacent carbon atom, permitting the electrons to pair and an additional π bond to be formed.
- The overlap in benzene is not limited to a pair of *p* orbitals, the *p* orbital of any one carbon atom overlap equally well the *p* orbitals of both carbon atoms to which it is bonded.
- The result is two continuous doughnut-shaped electron clouds, one lying above and the other below the plane of the atoms.





Doughnut-shaped cloud of π electrons

Aromaticity and Benzene

- The overlap of the *p* orbitals in both directions, and the resulting participation of each electron in several bonds, corresponds to the description of the molecule as a resonance hybrid of two structures.
- Again it is the ***delocalization*** of the π electrons that makes the molecule more stable.
- The π electrons are particularly available to a reagent that is seeking electrons.
- The typical reactions of the benzene ring are those in which it serves as a source of electrons for electrophilic reagents.
- Because of the resonance stabilization of the benzene ring, these reactions lead to substitution, in which the aromatic character of the benzene ring is preserved.

Aromatic Characters: The Huckel 4n + 2 rules

- We have defined aromatic compounds as those resemble benzene.
- Beside the compounds that contain benzene rings, there are many other substances that are called aromatic, yet some of these bear little resemblance to benzene.
- *Then, what properties do all aromatic compounds have in common?*
- From the experimental standpoint, aromatic compounds have a **high degree of unsaturation**, and are **resistant to the addition reactions** generally characteristic of unsaturated compounds.

Aromaticity and Benzene

- Instead of addition reactions, these aromatic compounds undergo electrophilic substitution reactions like those of benzene and are unusually stable.
- Aromatic compouds are cyclic, generally containing five-, six-, or seven-membered ring.
- When examined by physical methods they are found to have flat molecules.
- An aromatic compound has a molecular structure containing cyclic clouds of delocalized π electrons above and below the plane of the molecule, and the π clouds contain a total of (4n + 2) π electrons (where n is a whole number). This is known as **Huckel's rule**.

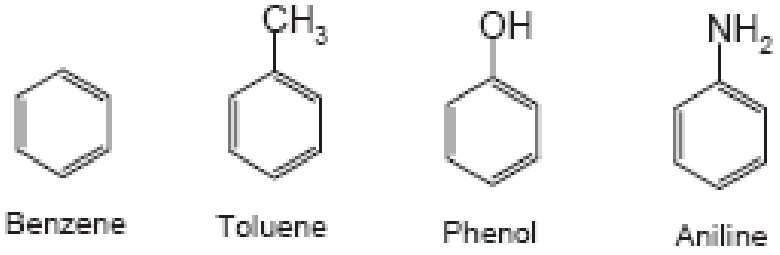
Aromaticity and Benzene

For example, benzene is an aromatic compound.

- If n = 1, we have 4 x 1 + 2 = 6, which means that any compound containing a total number of six π electrons is an aromatic compound.
- In the structure of benzene, there are three double bonds and six π electrons, and it is a planar molecule.
- Thus, benzene follows Huckel's rule, and is an aromatic compound.

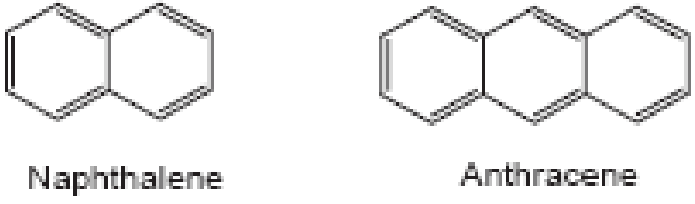
Classification of aromatic compounds

- **Benzene and its monocylic derivatives**



- **Polycyclic benzenoids**

  These aromatic compounds have two or more benzene rings fused together, e.g. naphthalene and anthracene.



- **Nonbenzenoids**

  These compounds generally have two or more rings fused together, but none of the rings is a benzene structure.

  They conform to Huckel's rule, i.e. they have (4n + 2) π electrons, and are aromatic compounds, e.g. azulene.



Azulene

In the above structure of azulene, there are five conjugated double bonds and ten π electrons, which means that it follows Huckel's rule (4 x 2 + 2 = 10).

- **Heterocyclic**

  These are compounds having at least one hetero atom (atom other than carbon, e.g. O, N and S) within the ring, and conforming to Huckel's rule.

  The examples of aromatic heterocyclic compounds are pyridine and pyrrole.

