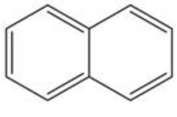
AROMATIC HYDROCARBONS

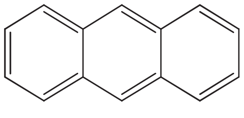
Aromatic hydrocarbons are often called 'arenes.' They get their name because many of them have a pleasant smell (derived from the Greek word "aroma," meaning pleasant smelling). These compounds are generally referred to as 'aromatic compounds.' Most of them feature a benzene ring, which is highly unsaturated. In most reactions involving aromatic compounds, the unsaturated nature of the benzene ring is preserved. However, there are instances of aromatic hydrocarbons that don't include a benzene ring but have a highly unsaturated ring. Aromatic compounds with a benzene ring are called benzenoids, while those without a benzene ring are termed non-benzenoids.

Here are some examples of arenes:

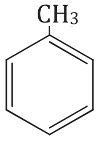
Benzene



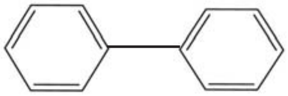
Naphthalen



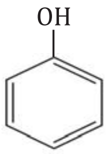
Anthracene



Toluene

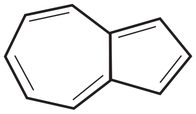


Biphenyl



Phenol

Because all of these compounds have benzene rings, they are classified as 'benzenoids'.

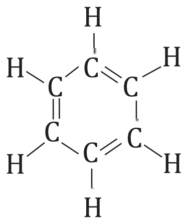


Azulene

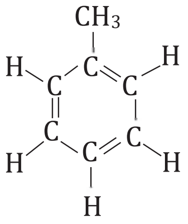
Even though azulene has aromatic characteristics, it is distinct from benzene, so it is considered a non-benzenoid aromatic compound.

Nomenclature and Isomerism

Since all six hydrogen atoms in benzene are the same, it only forms one type of monosubstituted product. However, when two hydrogen atoms are replaced by similar or different atoms or groups, three different position isomers can result, showing a difference in the placement of substituents. This means that disubstituted products of benzene exhibit position isomerism. The three possible isomers are 1,2 or 1,6 (referred to as ortho, o-), 1,3 or 1,5 (referred to as meta, m-), and 1,4 (referred to as para, p-) disubstituted compounds.

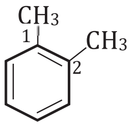


Benzene (C_6H_6)
with all the hydrogen atoms

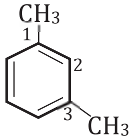


Methylbenzene (Toluene)

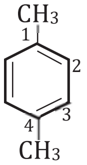
When a hydrogen atom is replaced by a methyl group, it results in a monosubstituted product. The dimethylbenzene has three different position isomers.



1, 2-Dimethyl benzene or
o-Dimethylbenzene or
o-Xylene



1, 3-Dimethylbenzene or
m-Dimethylbenzene or
m-Xylene



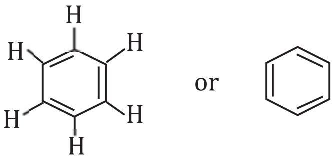
1, 4-Dimethyl benzene or
p-Dimethylbenzene or
p-Xylene

Structure of Benzene

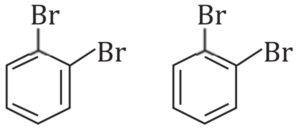
In 1825, Michael Faraday isolated benzene. Its molecular formula, C_6H_6, suggests high unsaturation, with eight fewer hydrogen atoms than the normal alkane C_6H_{14}. However, this formula didn't reveal its connection to alkanes, alkenes, or alkynes. Determining its structure was challenging. The formation of a triazolide, adding nine oxygen atoms during ozonolysis, hinted at three double bonds. Confirming this, when benzene was reduced with dihydrogen to form cyclohexane, six hydrogen atoms were added, indicating the presence of three double bonds.

$$C_6H_6 + 3H_2 \xrightarrow[200\text{-}250^\circ C]{Ni} \underset{\text{Cyclohexan}}{C_6H_{12}}$$

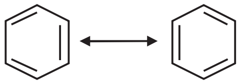
Benzene was discovered to only create a single type of monosubstituted derivative, suggesting that all six carbon and six hydrogen atoms in benzene are identical. Based on this finding, August Kekule proposed a structure for benzene in 1865. This structure involves a circular arrangement of six carbon atoms with alternating single and double bonds, each carbon atom having one hydrogen atom attached.



The Kekule structure suggests that there could be two different versions of 1,2-dibromobenzene. In one version, there's a single bond between the substituted carbon atoms, while in the other version, there's a double bond.



Yet, benzene was observed to produce just one ortho disubstituted product. This challenge was resolved by proposing the idea of the alternating nature of double bonds in benzene, as explained below:



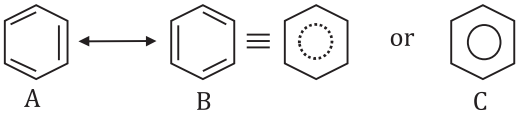
Despite the changes to the theory, Kekune couldn't clarify why benzene is unusually stable and tends to undergo substitution rather than addition reactions. This was later explained by the concept of resonance.

Resonance and Stability of Benzene

Two contemporary ideas have been proposed to clarify the stability and arrangement of benzene. These two concepts are:

Resonance or valence-bond theory

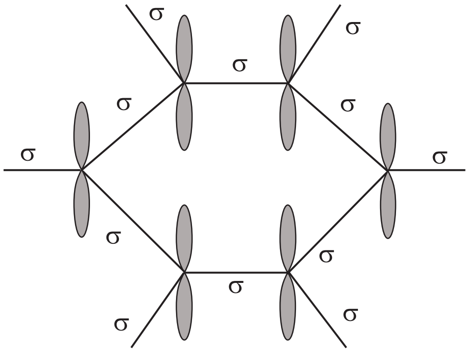
In valence-bond theory, the idea of double bonds in benzene, which used to be described as constantly switching places (as suggested by Kekune), is now explained through resonance. Even though the double bonds constantly shift, the resulting structures ensure that the position of the nucleus stays consistent in each one. The structural formula of this compound is a mix (hybrid) of the different proposed formulas. This condition is referred to as Resonance hybrid.



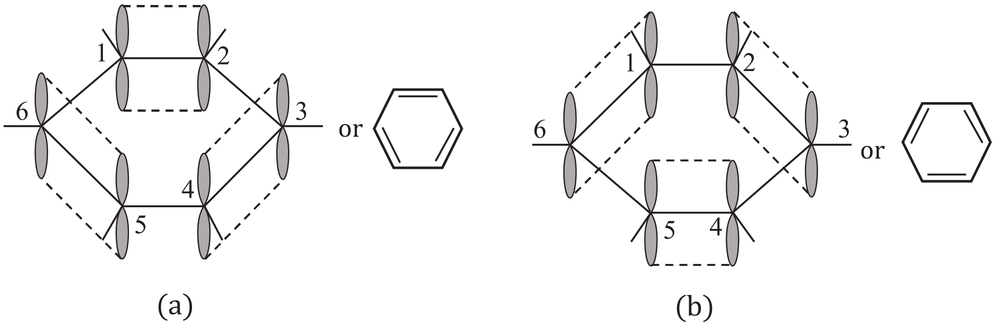
Kekule's suggested structures are the primary contributors to benzene's makeup. The combined structure is illustrated by adding a circle or dotted line inside the hexagon, as seen in figure (C). This circle symbolizes the six electrons that spread out between the six carbon atoms in the benzene ring.
X-ray diffraction data shows that benzene is a flat molecule. If either of the structures of benzene (A and B) had been accurate, we would have expected two different lengths for the carbon-carbon (C-C) bonds. However, X-ray data indicates that all six C-C bond lengths are approximately the same (139 pm), which falls between the lengths of a C-C single bond (154 pm) and a C-C double bond (133 pm). The C-C bond length in benzene (139 pm) suggests that each bond in benzene has taken on characteristics differently due to resonance. The single bond adopts some traits of a double bond, and the double bond takes on some traits of a single bond, causing changes in bond lengths. This explains why benzene, lacking a pure double bond, is hesitant to undergo addition reactions under normal conditions, elucidating its unusual behavior.

Valence bond theory to explain benzene structure:

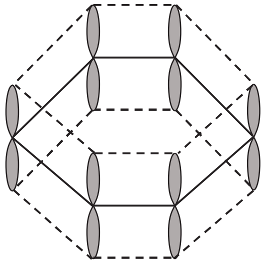
Orbital overlap helps us understand the structure of benzene more clearly. In benzene, all six carbon atoms have sp^2 hybridization. The sp^2 hybrid orbitals of neighboring carbon atoms overlap with each other, and they also overlap with the s-orbital of a hydrogen atom, forming six C-H sigma bonds. Each carbon atom now has one unhybridized p-orbital that sticks out perpendicular to the ring's plane, as depicted below:



The unhybridized p-orbitals of carbon atoms are near each other and can create a π-bond through side-to-side overlap. There are two equally likely ways to form three π-bonds by overlapping the p-orbitals of C_1 - C_2, C_3 - C_4, C_5 - C_6, or C_2 - C_3, C_4 - C_5, C_6 - C_1, as illustrated in the figures below.

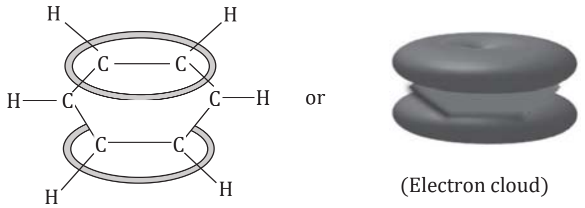


The figures above depict structures that match two of Kekule's structures with localized π-bonds. X-ray diffraction reveals that the distance between all carbon atoms in the ring is consistent, indicating an equal chance for the p-orbital of each carbon atom to overlap with the p-orbitals of neighboring carbon atoms. This overlap can be represented as two doughnuts (rings) of electron clouds, with one above the hexagonal ring's plane and one below it, as shown below:



(c)

The six π-electrons are spread out and can move around the six carbon nuclei, unlike the two electrons shown in (a) and (b). This scattering of electrons in a ring shape above and below the carbon atoms' plane is referred to as the delocalization of electrons.



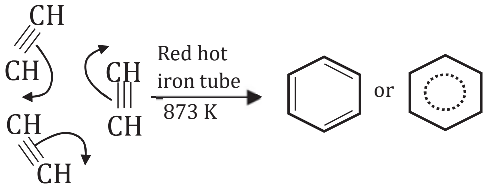
Benzene is more stable than the imagined cyclohexatriene because it has delocalized electrons.

Preparation of Benzene

Benzene is typically obtained from coal tar in commercial processes. Nonetheless, it can also be produced in a laboratory using the following methods.

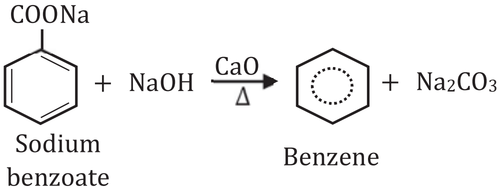
Cyclic polymerisation of ethyne

When ethyne is passed through a red-hot iron tube at 873 K, it goes through cyclic polymerization.



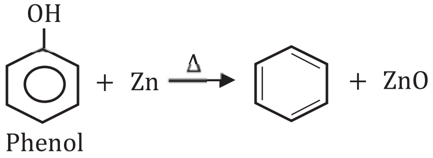
Decarboxylation of aromatic acids

When sodium benzoate, which is the sodium salt of benzoic acid, is heated with soda lime, it produces benzene.



Reduction of phenol

Benzene can be obtained by reducing phenol when its vapor is passed over heated zinc dust.



Physical Properties

Aromatic hydrocarbons are molecules without a specific polarity, often existing as colorless liquids or solids with a distinct smell. You might recognize naphthalene balls commonly used in toilets and for clothes preservation; they have a unique smell and act as moth repellents because they belong to the aromatic compound category. Aromatic compounds don't dissolve in water but can dissolve in organic solvents like alcohol and ether. When they burn, they produce a flame with soot.

Chemical Properties

Arenes are known for their electrophilic substitution reactions. However, in specific circumstances, they can also experience addition and oxidation reactions.