

AL- MUSTAQBAL UNIVERSITY

College Of Health And Medical Techniques

Prosthetic Dental Techniques Department

Second Grade

Second Semester



Advanced chemistry

Lecture 13 (The theoretical part)

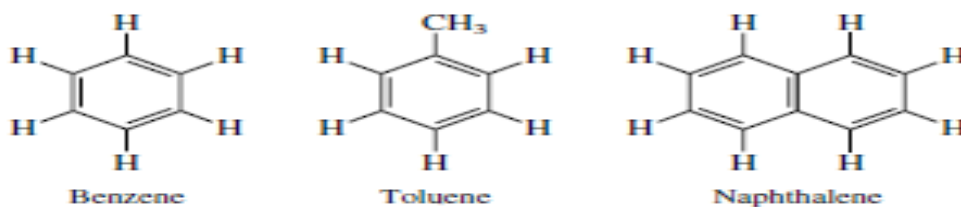
(Organic compounds (ARENES AND AROMATICITY))

By:

Assist.Prof.Dr.Ahmed A. AL-Khafagi

ARENES AND AROMATICITY

Arenes are hydrocarbons based on the benzene ring as a structural unit. Benzene, toluene, and naphthalene, for example, are arenes.



One factor that makes conjugation in arenes special is its cyclic nature. A conjugated system that closes upon itself can have properties that are much different from those of open-chain polyenes. Arenes are also referred to as **aromatic hydrocarbons**. Used in this sense, the word “**aromatic**” has nothing to do with odor but means instead that arenes are much more stable than we expect them to be based on their formulation as conjugated trienes.

Of **aromaticity**—to see what are the properties of benzene and its derivatives that reflect its special stability, and to explore the reasons for it. This chapter develops the idea of the benzene ring as a fundamental structural unit and examines the effect of a benzene ring as a substituent. The chapter following this one describes reactions that involve the ring itself. Let’s begin by tracing the history of benzene, its origin, and its structure. Many of the terms we use, including *aromaticity* itself, are of historical origin. We’ll begin with the discovery of benzene.

9.1. BENZENE

In 1825, Michael Faraday isolated a new hydrocarbon from illuminating gas, which he called “bicarburet of hydrogen.” Nine years later Eilhardt Mitscherlich of the University of Berlin prepared the same substance by heating benzoic acid with lime and found it to be a hydrocarbon having the empirical formula C_nH_n .

Eventually, because of its relationship to benzoic acid, this hydrocarbon came to be named *benzin*, then later *benzene*, the name by which it is known today. Benzoic acid had been known for several hundred years by the time of Mitscherlich’s experiment. Many trees exude resinous materials called *balsams* when cuts are made in their bark. Some of these balsams are very fragrant, which once made them highly prized articles of commerce, especially when the trees that produced them could be found only in exotic, faraway lands. *Gum benzoin* is a balsam obtained from a tree that grows in Java and Sumatra. “Benzoin” is a word derived from the French equivalent, *benjoin*, which in turn comes from the Arabic *lubanjawi*, meaning “incense from Java.” Benzoic acid is itself odorless but can easily be isolated from gum benzoin. Compounds related to benzene were obtained

from similar plant extracts. For example, a pleasant-smelling resin known as *tolu balsam* was obtained from the South American tolu tree. In the 1840s it was discovered that distillation of tolu balsam gave a methyl derivative of benzene, which, not surprisingly, came to be named *toluene*. Although benzene and toluene are not particularly fragrant compounds themselves, their origins in aromatic plant extracts led them and compounds related to them to be classified as *aromatic hydrocarbons*. Alkanes, alkenes, and alkynes belong to another class, the **aliphatic hydrocarbons**. The word “aliphatic” comes from the Greek *aleiphar* (meaning “oil” or “unguent”) and was given to hydrocarbons that were obtained by the chemical degradation of fats. Benzene was prepared from coal tar by August W. von Hofmann in 1845. Coal tar remained the primary source for the industrial production of benzene for many years, until petroleum-based technologies became competitive about 1950. Current production is about 6 million tons per year in the United States. A substantial portion of this benzene is converted to styrene for use in the preparation of polystyrene plastics and films. Toluene is also an important organic chemical. Like benzene, its early industrial production was from coal tar, but most of it now comes from petroleum.

9.2. KEKULÉ AND THE STRUCTURE OF BENZENE

The classification of hydrocarbons as aliphatic or aromatic took place in the 1860s when it was already apparent that there was something special about benzene, toluene, and their derivatives. Their molecular formulas (benzene is C_6H_6 , toluene is C_7H_8) indicate that, like alkenes and alkynes, they are unsaturated and should undergo addition reactions. Under conditions in which bromine, for example, reacts rapidly with alkenes and alkynes, however, benzene proved to be inert. Benzene does react with Br_2 in the presence of iron(III) bromide as a catalyst, but even then addition isn't observed. Substitution occurs instead

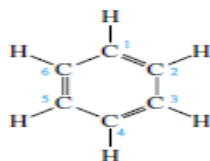


Furthermore, only one monobromination product of benzene was ever obtained, which suggests that all the hydrogen atoms of benzene are equivalent. Substitution of one hydrogen by bromine gives the same product as substitution of any of the other hydrogens. Chemists came to regard the six carbon atoms of benzene as a fundamental structural unit. Reactions could be carried out that altered its substituents, but the integrity of the benzene unit remained undisturbed. There

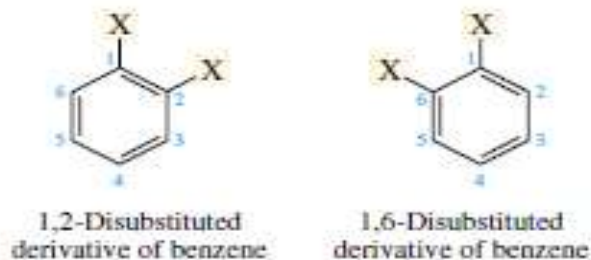
must be something “special” about benzene that makes it inert to many of the reagents that add to alkenes and alkynes. In 1866, only a few years after publishing his ideas concerning what we now recognize as the structural theory of organic chemistry, August Kekulé applied it to the structure of benzene. He based his reasoning on three premises:

1. Benzene is C_6H_6 .
2. All the hydrogens of benzene are equivalent.
3. The structural theory requires that there be four bonds to each carbon.

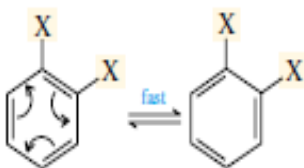
Kekulé advanced the venturesome notion that the six carbon atoms of benzene were joined together in a ring. Four bonds to each carbon could be accommodated by a system of alternating single and double bonds with one hydrogen on each carbon.



A flaw in Kekulé's structure for benzene was soon discovered. Kekulé's structure requires that 1,2- and 1,6-disubstitution patterns create different compounds (isomers).



The two substituted carbons are connected by a double bond in one but by a single bond in the other. Since no such cases of isomerism in benzene derivatives were known, and none could be found, Kekulé suggested that two isomeric structures could exist but interconverted too rapidly to be separated.

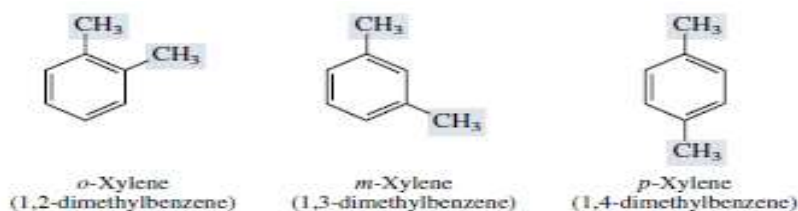


9.3.SUBSTITUTED DERIVATIVES OF BENZENE AND THEIR NOMENCLATURE

All compounds that contain a benzene ring are aromatic, and substituted derivatives of benzene make up the largest class of aromatic compounds. Many such compounds are named by attaching the name of the substituent as a prefix to *benzene*.



Many simple monosubstituted derivatives of benzene have common names of long standing that have been retained in the IUPAC system. Table 5 lists some of the most important ones. Dimethyl derivatives of benzene are called *xylenes*. There are three xylene isomers, the *ortho* (*o*-), *meta* (*m*-), and *para* (*p*-) substituted derivatives.



The prefix *ortho* signifies a 1,2-disubstituted benzene ring, *meta* signifies 1,3-disubstitution, and *para* signifies 1,4-disubstitution. The prefixes *o*, *m*, and *p* can be used when a substance is named as a benzene derivative or when a specific base name (such as acetophenone) is used. For example

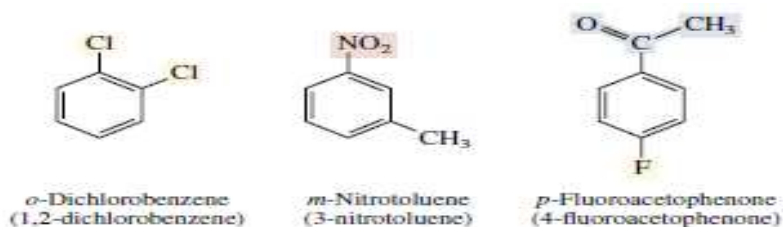
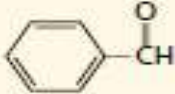
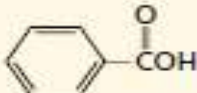
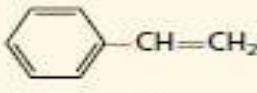
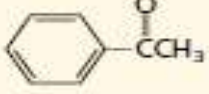
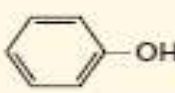
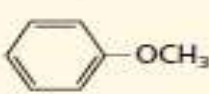
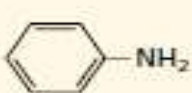


TABLE 5 Names of Some Frequently Encountered Derivatives of Benzene

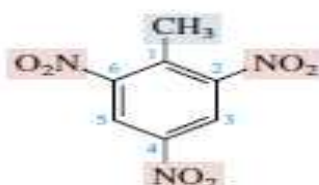
| Structure | Systematic Name | Common Name* |
|------------------------------------------------------------------------------------|------------------------|--------------|
|  | Benzenecarbaldehyde | Benzaldehyde |
|  | Benzenecarboxylic acid | Benzoic acid |
|  | Vinylbenzene | Styrene |
|  | Methyl phenyl ketone | Acetophenone |
|  | Benzenol | Phenol |
|  | Methoxybenzene | Anisole |
|  | Benzenamine | Aniline |

*These common names are acceptable in IUPAC nomenclature and are the names that will be used in this text.

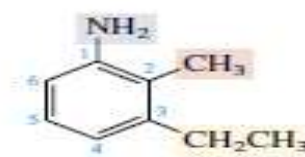
The prefixes o, m, and p are not used when three or more substituents are present on benzene; numerical locants must be used instead.



4-Ethyl-2-fluoroanisole



2,4,6-Trinitrotoluene

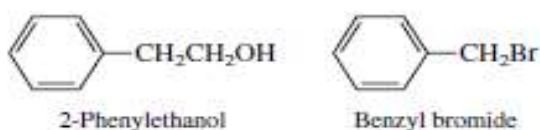


3-Ethyl-2-methylaniline

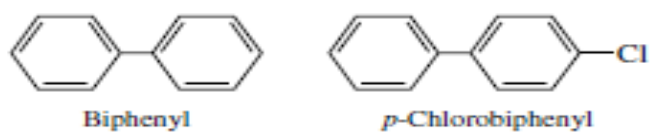
In these examples the base name of the benzene derivative determines the carbon at which numbering begins: anisole has its methoxy group at C-1, toluene its methyl group at C-1, and aniline its amino group at C-1. The direction of numbering is chosen to give the next substituted position the lowest number irrespective of what substituent it bears. *The order of appearance of substituents in the name is alphabetical.* When no simple base name other than benzene is appropriate, positions are numbered so as to give the lowest locant at the first point of difference. Thus, each of the following examples is named as a 1,2,4-trisubstituted derivative of benzene rather than as a 1,3,4-derivative:



When the benzene ring is named as a substituent, the word “phenyl” stands for C_6H_5- . Similarly, an arene named as a substituent is called an *aryl* group. A *benzyl* group is $C_6H_5CH_2-$.



Biphenyl is the accepted IUPAC name for the compound in which two benzene rings are connected by a single bond.

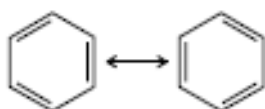


9.4.SUMMARY

1-Benzene is the parent of a class of hydrocarbons called **arenes**, or **aromatic hydrocarbons**.

2-An important property of aromatic hydrocarbons is that they are much more stable and less reactive than other unsaturated compounds. Benzene, for example, does not react with many of the reagents that react rapidly with alkenes. When reaction does take place, substitution rather than addition is observed. The Kekulé formulas for benzene seem inconsistent with its low reactivity and with the fact that all of the C-C bonds in benzene are the same length (140 pm).

3-One explanation for the structure and stability of benzene and other arenes is based on resonance, according to which benzene is regarded as a hybrid of the two Kekulé structures.



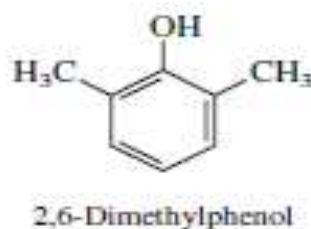
4-The extent to which benzene is more stable than either of the Kekulé structures is its **resonance energy**, which is estimated to be 125–150 kJ/mol (30–36 kcal/mol) from heats of hydrogenation data.

5-According to the orbital hybridization model, benzene has six π electrons, which are shared by all six sp^2 -hybridized carbons. Regions of high π electron density are located above and below the plane of the ring.



6-A molecular orbital description of benzene has three π orbitals that are bonding and three that are antibonding. Each of the bonding orbitals is fully occupied (two electrons each), and the antibonding orbitals are vacant.

7-Many aromatic compounds are simply substituted derivatives of benzene and are named accordingly. Many others have names based on some other parent aromatic compound.





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Lecture (11)

(الكيمياء العضوية)

(Organic compounds)

- ARENES AND AROMATICITY
- BENZENE
- THE STRUCTURE OF BENZENE
- SUBSTITUTED DERIVATIVES OF BENZENE AND THEIR NOMENCLATURE
- SUMMARY

BY

Ahmed Adnan Abdul Ameer

Ph.DSc.s . M.Sc. B.Sc.

Analytical chemistry

FIA

2017-3- 29