Organic Chemistry I

Mohammad Jafarzadeh Faculty of Chemistry, Razi University

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Organic Chemistry, (9th edition)

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5. Benzene and Aromaticity

Aromatic to refer to the class of compounds that contain six-membered benzene-like rings with three double bonds.

Naming Aromatic Compounds

Simple aromatic hydrocarbons come from two main sources: coal and petroleum. Coal is a complex mixture consisting primarily of large arrays of conjoined benzene-like rings. Thermal breakdown of coal occurs when it is heated to 1000 °C in the absence of air, and a mixture of volatile products called *coal tar* boils off. Fractional distillation of coal tar yields benzene, toluene, xylene (dimethylbenzene), naphthalene, and other aromatic compounds



Aromatic substances have acquired a large number of nonsystematic names. IUPAC rules discourage the use of most such names but do allow some of the more widely used ones to be retained. Methylbenzene is known commonly as *toluene;* hydroxybenzene as *phenol;* aminobenzene as *aniline*.

MBEE 19 1 Common Maines of Some Monnaile Compounds			
Structure	Name	Structure	Name
CH ₃	Toluene (bp 111 °C)	СНО	Benzaldehyde (bp 178 °C)
ОН	Phenol (mp 43 °C)	CO ₂ H	Benzoic acid (mp 122 °C)
NH ₂	Aniline (bp 184 °C)	CH ₃ CH ₃	<i>ortho</i> -Xylene (bp 144 °C)
CH3	Acetophenone (mp 21 °C)	H C C H H	Styrene (bp 145 °C)

Monosubstituted benzenes are named systematically in the same manner as other hydrocarbons, with *-benzene* as the parent name.



Alkyl-substituted benzenes are sometimes referred to as **arenes** and are named in different ways depending on the size of the alkyl group.

If the alkyl substituent is smaller than the ring (six or fewer carbons), the arene is referred to as an **alkyl-substituted benzene**. If the alkyl substituent is larger than the ring (seven or more carbons), the compound is referred to as a **phenyl-substituted alkane**.

The name **phenyl**, abbreviated as Ph or Φ , is used for the $-C_6H_5$ unit when the benzene ring is considered a substituent.

In addition, the name **benzyl** is used for the $C_6H_5CH_2$ – group.



Disubstituted benzenes are named using the prefixes **ortho** (*o*), **meta** (*m*), or **para** (*p*). An ortho-disubstituted benzene has its two substituents in a 1,2 relationship on the ring, a meta-disubstituted benzene has its two substituents in a 1,3 relationship, and a para-disubstituted benzene has its a 1,4 relationship.



The ortho, meta, para system of nomenclature is also useful when discussing reactions. For example, the reaction of bromine with toluene is said, "Reaction occurs at the para position":



As with cycloalkanes, benzenes with more than two substituents are named by choosing a point of attachment as carbon 1 and numbering the substituents on the ring so that the second substituent has as low a number as possible. The substituents are listed alphabetically when writing the name.



Structure and Stability of Benzene

Benzene (C_6H_6) has six fewer hydrogens than the corresponding six-carbon cycloalkane (C_6H_{12}) and is clearly unsaturated, usually being represented as a six-membered ring with alternating double and single bonds.

Yet it has been known since the mid-1800s that benzene is much less reactive than typical alkenes and fails to undergo typical alkene addition reactions.

Cyclohexene reacts rapidly with Br_2 and gives the addition product 1,2-dibromocyclohexane, but benzene only reacts slowly with Br_2 and gives the *substitution* product C_6H_5Br .



Benzene's stability by measuring heats of hydrogenation: cyclohexene, an isolated alkene, has $\Delta H^{\circ}_{hydrog} = -118$ kJ/mol (-28.2 kcal/mol), and 1,3-cyclohexadiene, a conjugated diene, has $\Delta H^{\circ}_{hydrog} = -230$ kJ/mol (-55.0 kcal/mol). This value for 1,3-cyclohexadiene is less than twice that for cyclohexene because conjugated dienes are more stable than isolated dienes.

 $\Delta H^{\circ}_{hydrog}$ for "cyclohexatriene" (benzene) is expected to be a bit less than -356 kJ/mol, or three times the cyclohexene value. The actual value is -206 kJ/mol, 150 kJ/mol (36 kcal/mol) less than expected. Benzene is more stable than expected by 150 kJ/mol.



Further evidence for the unusual nature of benzene is that all its carbon–carbon bonds have the same length—139 pm—intermediate between typical single (154 pm) and double (134 pm) bonds.

In addition, an electrostatic potential map shows that the electron density in all six C-C bonds is identical. Thus, benzene is a planar molecule with the shape of a regular hexagon.

All C-C-C bond angles are 120°, all six carbon atoms are sp^2 -hybridized, and each carbon has a *p* orbital perpendicular to the plane of the six-membered ring.





Because all six carbon atoms and all six p orbitals in benzene are equivalent, it's impossible to define three localized π bonds in which a given p orbital overlaps only one neighboring p orbital. Rather, each p orbital overlaps equally well with both neighboring p orbitals, leading to a picture of benzene in which all six π electrons are free to move about the entire ring.

In resonance terms, benzene is a hybrid of two equivalent forms. Neither form is correct by itself; the true structure of benzene is somewhere in between the two resonance forms but is impossible to draw with our usual conventions.

