

Chapter 15: Benzene & Aromaticity

Learning Objective & Key Concepts

1. Sources and nomenclature of aromatic compounds.
2. Introduction to Huckel $4n+2$ rule and aromaticity – stability and reactivity,
3. Introduction to aromatic heterocycles and polycyclic aromatic compounds
4. Key spectroscopy characteristics of aromatic compounds

Keywords: *Aromatic, aliphatic, Huckel Rule, aromaticity, heterocyclic compounds, polycyclic compounds*

Tutorial Questions

These are a subset of EOC questions, hand these in for extra credit, but I strongly advise you to complete the full set of EOC questions as well as in-text questions too.

15.18 15.20 15.21 15.41

End-of-Chapter Problems

15.13
15.18, 15.20, 15.21 – Good practice for nomenclature.
15.31 – interesting one for discussion.

After we've completed spectroscopy lecture course, try also:

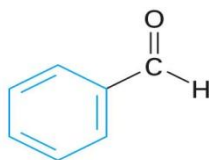
15.41
15.44
15.46

Before systematic nomenclature was introduced, many compounds were labeled “**aromatic**” because of their strong fragrance. Today, aromatic compounds are ones which have benzene and/or benzene like rings in their structure. Since structure profoundly dictates reactivity and property, it is important to examine the structure of aromatic compounds before embarking on a study of their reactivity and properties. Chapter 15 focuses on the structural features of aromatic compounds and chapter 16 looks at some key reactions of aromatic compounds. As we’ll see in this and the next chapter, aromatic compounds have distinctly different properties and reactivity compared to the **aliphatic** (non-aromatic) compounds we’ve seen so far.

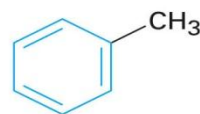
Examples of aromatic compounds:



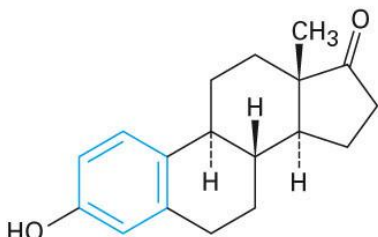
Benzene
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Benzaldehyde

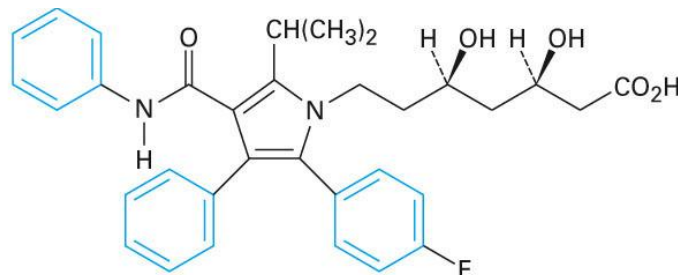


Toluene



Estrone

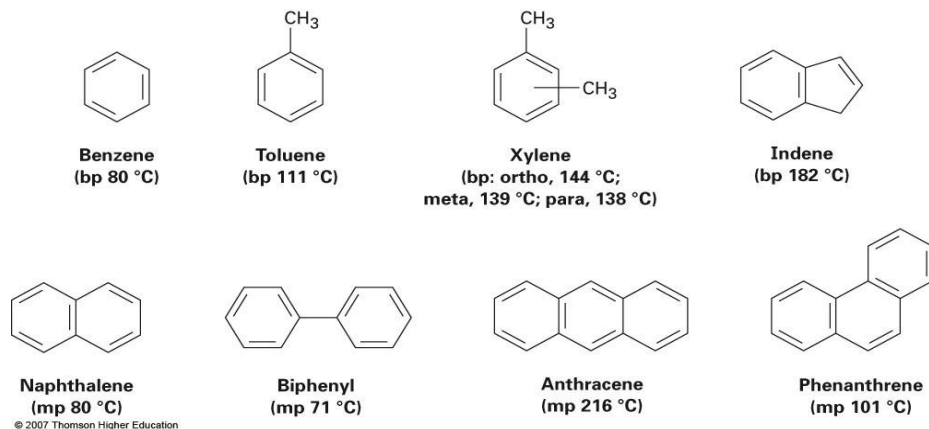
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**Atorvastatin
(Lipitor)**

15.1 Sources and Names of Aromatic Compounds

Coal and petroleum form the main sources of aromatic compounds. The simplest aromatics such as benzene, toluene, xylene and naphthalene are mostly formed during fractional distillation of coal tar.



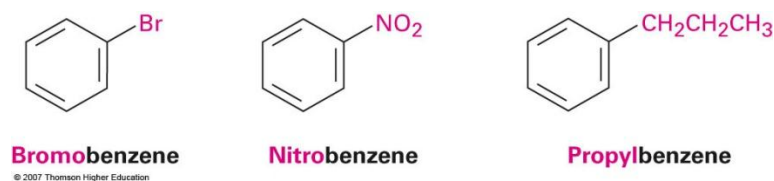
Many aromatic compounds are still known by their common names. You are expected to know at least the following common names in addition to systematic (IUPAC) names.

Table 15.1 Common Names of Some Aromatic Compounds

Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		ortho-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

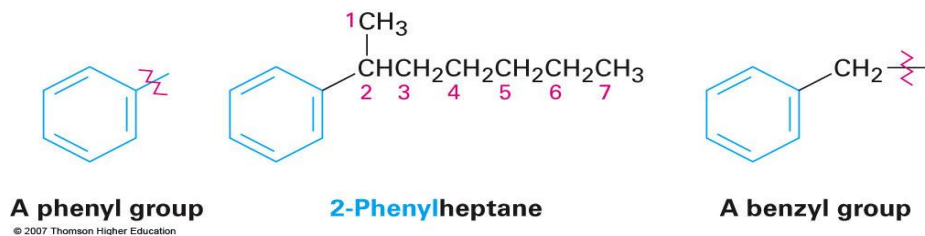
IUPAC aromatic nomenclature is complicated, we will look only at monosubstituted and disubstituted and a few trisubstituted benzenes.

Monosubstituted benzenes are named with “-benzene” as parents:

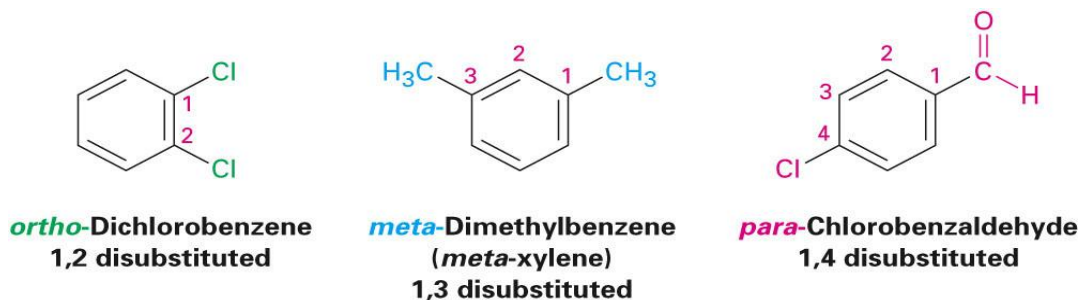


Alkyl benzenes are sometimes called **arenes**. Whether the benzene ring or a substituent is the parent depends on relative size of the alkyl group. So “propyl benzene” because propyl has less carbon than the benzene ring, but “2-phenylheptane” because heptane has more carbon atoms than a benzene ring.

Note the phenyl and the benzyl group (analogous to alkyl groups)



Disubstituted benzenes have prefixes for the relative positions of the two substituent groups: **ortho** (o), **meta** (m) and **para** (p). These correspond to the 1,2-, 1,3- and 1,4-positions respectively.



For benzenes with more than two substituents: choose a point of attachment as carbon 1 and number the ring in a direction to give the second lowest number as possible. The substituents are then listed in alphabetical order (ignoring prefixes such as di-, tri-).



❖ Try problem 15.1

❖ Try problem 15.2

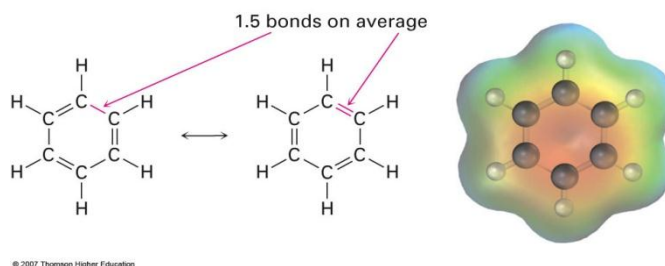
❖ Try problem 15.3

15.2 Structure and Stability of Benzene: Molecular Orbital Theory

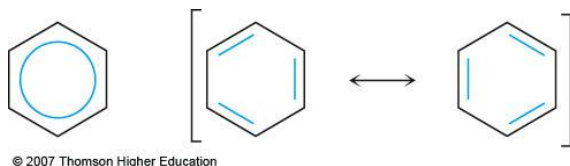
Although a benzene ring has C=C double bonds, it does NOT behave like an alkene. Instead of electrophilic addition, a benzene ring undergoes substitution where the benzene ring structure is preserved:



This and other properties – thermodynamic data, bond angle and bond enthalpy values – led chemists to eventually define “aromaticity” – the property of “being aromatic”. (See textbook for more detail)



Structural drawings for benzene: either as a ring or as alternating double bonds. (We will usually use the cyclohexatriene symbol because it's easier to use with curly arrows in mechanisms)



Alternative representations of benzene. The “circle” representation must be used carefully since it doesn't indicate the number of π electrons in the ring.

15.3 Aromaticity and the Huckel $4n+2$ rule

(See textbook for more detail)

By 1930's, chemists began to investigate what structural features are common in aromatic compounds and help explain their unique property of “aromaticity”. A lot of this was done by the German Physicist Erich Huckel, his key conclusions are:

Aromatic compounds are planar, cyclic systems of conjugation and contains $4n+2$ π electrons where n is any integer.

Aromatic rings are very stable. In reaction, the π -electron ring system is usually conserved and the reaction is substitution rather than addition.

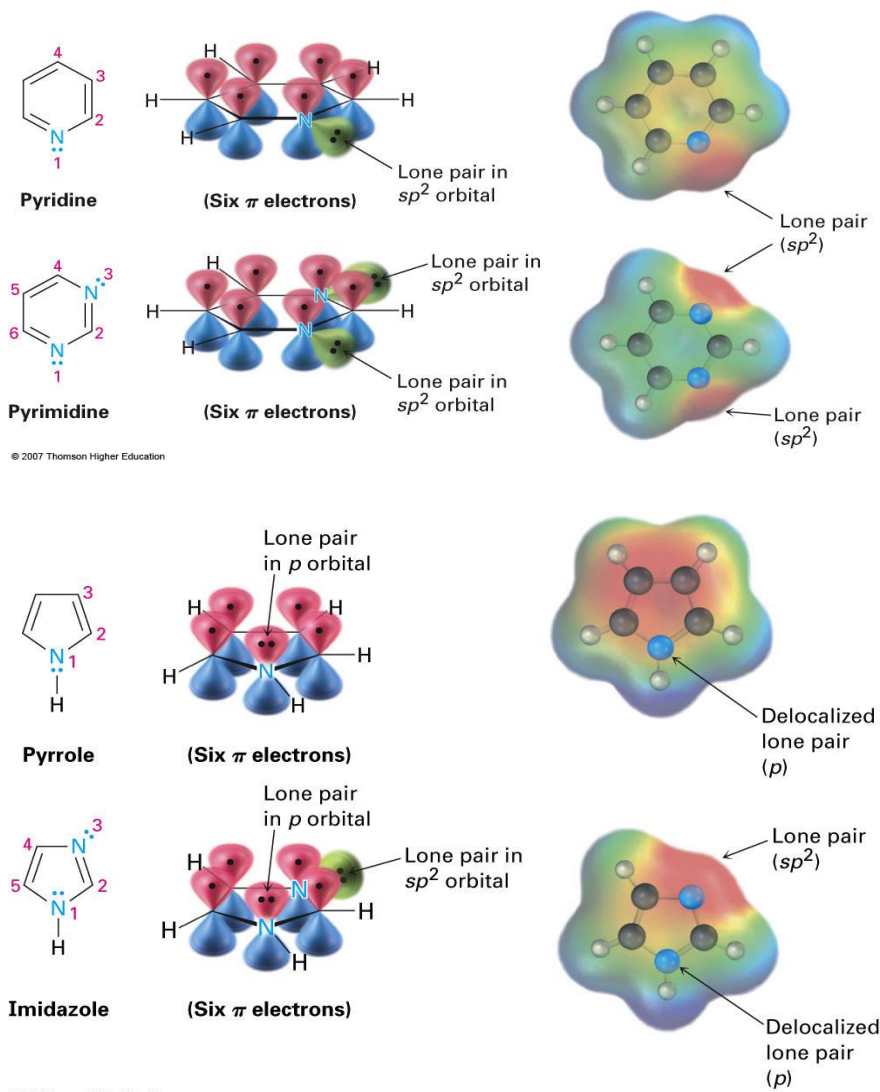
**In other words: 6, 10, 14, 18, 22 etc. This is known as “Huckel's $4n+2$ rule”*

15.4 Aromatic Ions

(Skip this section)

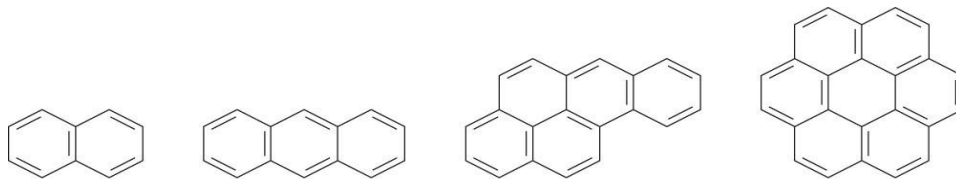
15.5 Aromatic Heterocycles: Pyridine and Pyrrole

Aromatic compounds may contain heteroatoms in the aromatic ring. Two widely occurring examples are pyridine and pyrrole. Examine each one and make sure they meet requirement for aromaticity (planar, conjugate π -electron system, $4n+2$).

15.6 Why $4n+2$ *Skip this section*

15.7 Polycyclic Aromatic Compounds

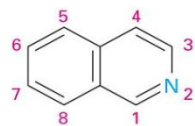
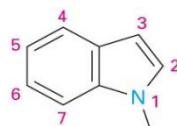
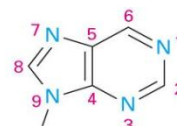
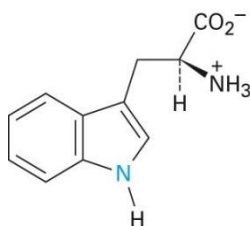
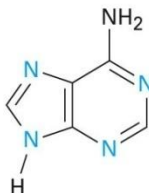
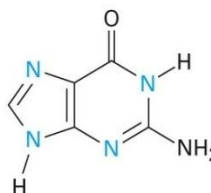
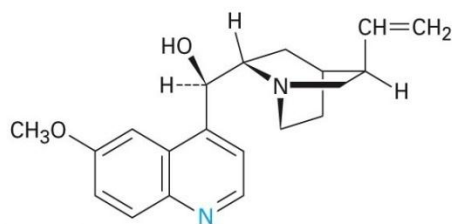
Aromatic compounds may also be polycyclic. Examples are shown here. You do not need to memorize these structures but look out for them both in chemistry and in biochemical systems.

**Naphthalene**

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Anthracene**Benzo[a]pyrene****Coronene****Quinoline**

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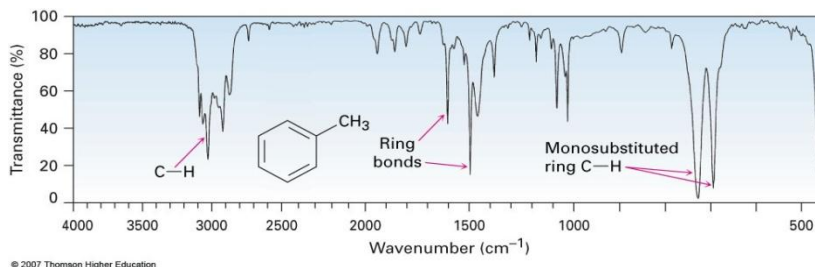
**Isoquinoline****Indole****Purine****Tryptophan**
(an amino acid)**Adenine**
(in DNA and RNA)**Guanine**
(in DNA and RNA)**Quinine**
(an antimalarial agent)

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15.8 Spectroscopy of Aromatic Compounds

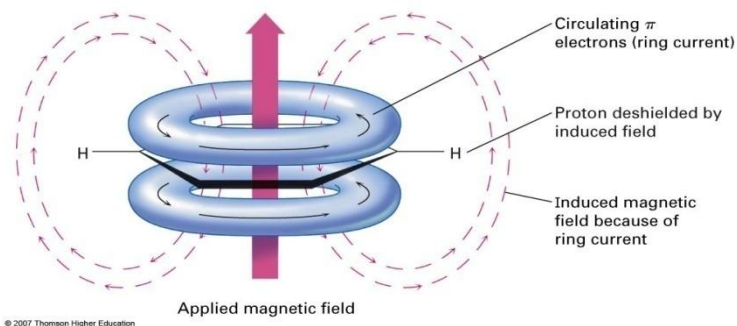
Spectroscopy is covered in earlier chapters. Here, we will just summarize the key spectroscopy features of aromatic compounds:

Infra Red:

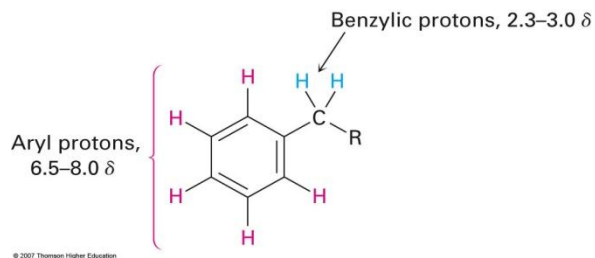


$^1\text{H NMR}$:

Aromatic hydrogens are strongly deshielded due to the ring-current effect of the π -electron ring.



Aromatic hydrogens have chemical shifts in the 6.5 – 8.0 δ range, compared to 4.5-6.5 δ for vinyl hydrogens. The ring-effect also accounts for the greater deshielding of protons in the benzylic position compared to other alkane protons.



$^{13}\text{C NMR}$:

The ring effect is less pronounced in the case of ^{13}C spectrum, chemical shifts for benzene carbons have a range of 110 to 140 ppm, making it hard to distinguish from alkene carbons.