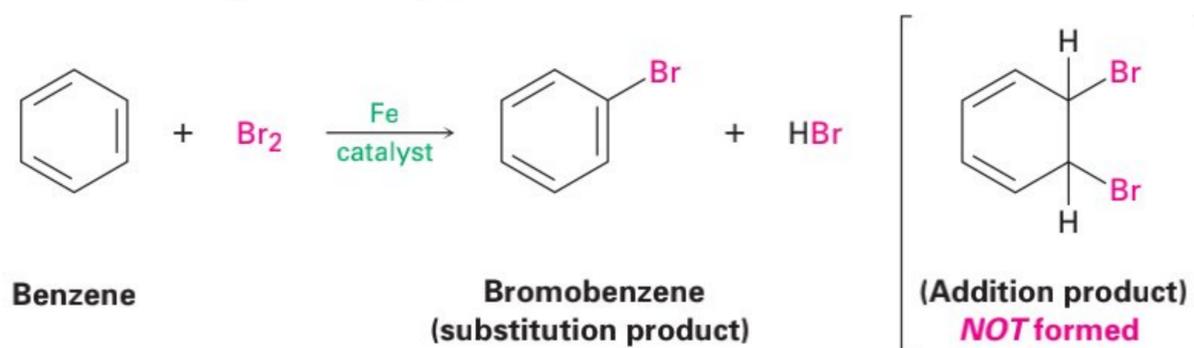


WHY THIS CHAPTER?

Aromatic rings are a common part of many organic structures and are particularly important in nucleic acid chemistry and in the chemistry of several amino acids. In this chapter, we'll find out how and why aromatic compounds are different from such apparently related compounds as alkenes.

5.1 Structure of Benzene

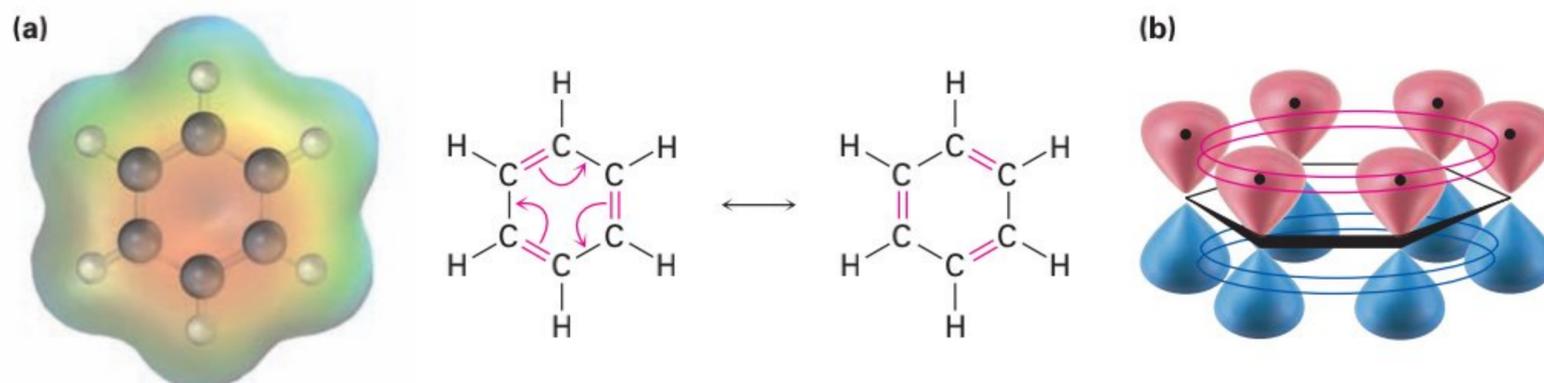
Benzene (C_6H_6) has eight fewer hydrogens than the corresponding six-carbon alkane (C_6H_{14}) and is clearly unsaturated, usually being represented as a six-membered ring with alternating double and single bond. Yet it has been known since the mid-1800s that benzene is much less reactive than typical alkenes and fails to undergo typical alkene addition reactions. Cyclohexene, for instance, reacts rapidly with Br_2 and gives the addition product 1,2-dibromocyclohexane, but benzene reacts only slowly with Br_2 and gives the *substitution* product C_6H_5Br .



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, the electron density in all six carbon-carbon bonds is identical, as shown by an electrostatic potential map (Figure 5.1a). 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 (Figure 5.1b). In resonance terms (Sections 4.9 and 4.10), 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. Because of this resonance, benzene is more stable and less reactive than a typical alkene.

Figure 5.1 (a) An electrostatic potential map of benzene and (b) an orbital picture. Each of the six carbon atoms has a p orbital that can overlap equally well with neighboring p orbitals on both sides. The π electrons are thus shared around the ring in two doughnut-shaped clouds, and all C-C bonds are equivalent.



Problem 5.1

Line-bond structures appear to imply that there are two different isomers of 1,2-dibromobenzene, one with the bromine-bearing carbon atoms joined by a double bond and one with the bromine-bearing carbons joined by a single bond. In fact, though, there is only one 1,2-dibromobenzene. Explain.



5.2 Naming Aromatic Compounds

Aromatic substances, more than any other class of organic compounds, have acquired a large number of common names. IUPAC rules discourage the use of most such names but allow some of the more widely used ones to be retained (Table 5.1). Thus, methylbenzene is commonly known as *toluene*, hydroxybenzene as *phenol*, aminobenzene as *aniline*, and so on.

Table 5.1 Common Names of Some Aromatic Compounds

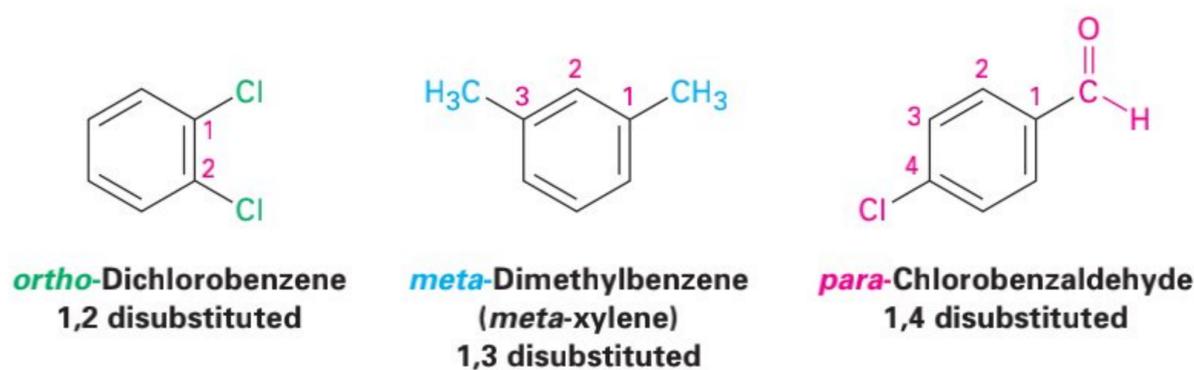
Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		<i>ortho</i> -Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

Monosubstituted benzenes are systematically named in the same manner as other hydrocarbons, with *-benzene* as the parent name. Thus, C_6H_5Br is bromobenzene, $C_6H_5NO_2$ is nitrobenzene, and $C_6H_5CH_2CH_3$ is ethylbenzene. The name **phenyl**, pronounced **fen**-nil and sometimes abbreviated as Ph or Φ (Greek phi), is used for the $-C_6H_5$ unit when the benzene ring is considered as a substituent. In addition, a generalized aromatic substituent is called an

aryl group, abbreviated as Ar, and the name **benzyl** is used for the $C_6H_5CH_2-$ group.



Disubstituted benzenes are named using one of 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 substituents in a 1,4 relationship.



As with cycloalkanes (Section 2.7), 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.



Note in the second and third examples shown that *-phenol* and *-toluene* are used as the parent names rather than *-benzene*. Any of the monosubstituted aromatic compounds shown in Table 5.1 can be used as a parent name, with the principal substituent ($-OH$ in phenol or $-CH_3$ in toluene) considered as C1.

Worked Example 5.1

Naming an Aromatic Compound

What is the IUPAC name of the following compound?

