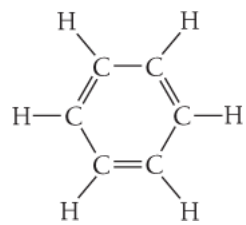
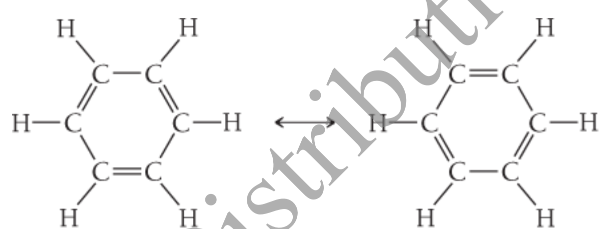
21.7: Aromatic Hydrocarbons

As you might imagine, determining the structure of organic compounds has not always been easy. During the mid-1800s, chemists were working to determine the structure of a particularly stable organic compound named benzene (C_6H_6). In 1865, Friedrich August Kekulé (1829–1896) had a dream in which he envisioned chains of carbon atoms as snakes. The snakes danced before him, and one of them twisted around and bit its tail. Based on that vision, Kekulé proposed the following structure for benzene:



This structure has alternating single and double bonds. When we examine the carbon–carbon bond lengths in benzene, however, we find that all the bonds are the same length, which indicates that the following resonance structures are a more accurate representation of benzene:

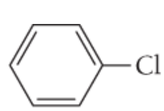


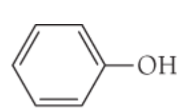
> Recall from Section 5.4 that the actual structure of a molecule represented by resonance structures is intermediate between the two resonance structures and is called a *resonance hybrid*.

The true structure of benzene is a hybrid of the two resonance structures. We often represent benzene with the following carbon skeletal formula (or line formula):

The ring represents the delocalized π electrons that occupy the molecular orbital shown superimposed on the ball-and-stick model. When drawing benzene rings, either by themselves or as parts of other compounds, organic chemists use either this diagram or just one of the resonance structures with alternating double bonds. Both representations indicate the same thing—a benzene ring.

The benzene ring structure occurs in many organic compounds. An atom or group of atoms can substitute for one or more of the six hydrogen atoms on the ring to form compounds referred to as *substituted benzenes,* such as chlorobenzene and phenol.



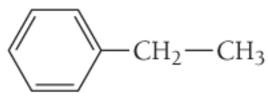


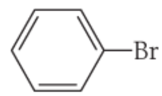
chlorobenzene phenol

Because many compounds containing benzene rings have pleasant aromas, benzene rings are also called *aromatic rings*, and compounds containing them are called *aromatic compounds*. Aromatic compounds are responsible for the pleasant smells of cinnamon, vanilla, and jasmine.

Naming Aromatic Hydrocarbons

Monosubstituted benzenes—benzenes in which only one of the hydrogen atoms has been substituted—are often named as derivatives of benzene.

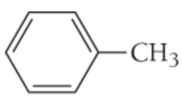

ethylbenzene

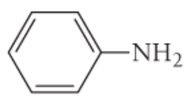

bromobenzene

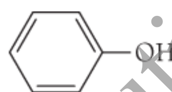
These names take the general form:

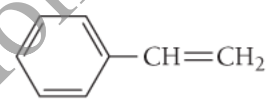
(name of substituent) benzene

However, many monosubstituted benzenes have names that can only be learned through familiarity. Some common ones are shown here:

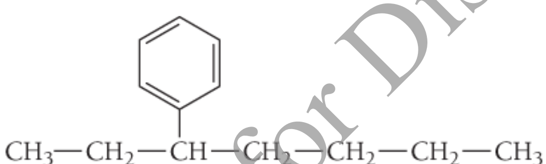

toluene

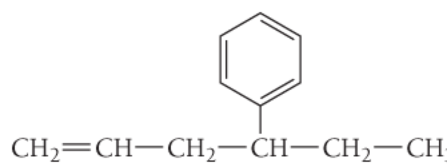

aniline


phenol

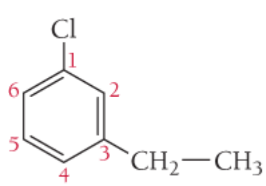

styrene

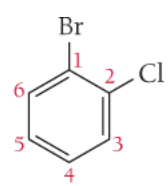
We name some substituted benzenes, especially those with large substituents, by treating the benzene ring as the substituent. In these cases, we refer to the benzene substituent as a **phenyl group**.


3-phenylheptane

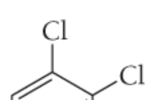

4-phenyl-1-hexene

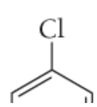
Disubstituted benzenes—benzenes in which two hydrogen atoms have been substituted—are numbered, and the substituents are listed alphabetically. We determine the order of numbering on the ring by the alphabetical order of the substituents.

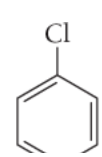

1-chloro-3-ethylbenzene

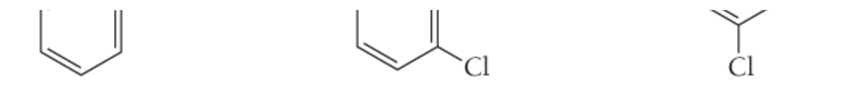

1-bromo-2-chlorobenzene

When the two substituents are identical, we use the prefix *di-*:



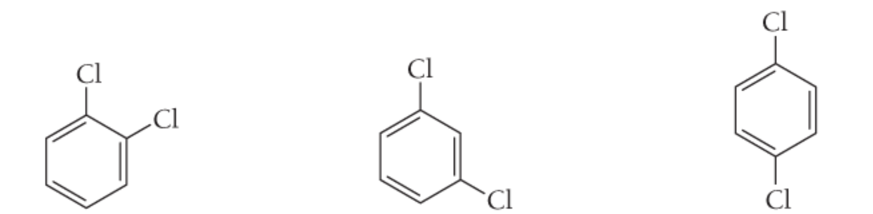






1,2-dichlorobenzene 1,3-dichlorobenzene 1,4-dichlorobenzene

Also in common use, in place of numbering, are the prefixes *ortho* (1,2 disubstituted), *meta* (1,3 disubstituted), and *para* (1,4 disubstituted):



ortho-dichlorobenzene or *o*-dichlorobenzene

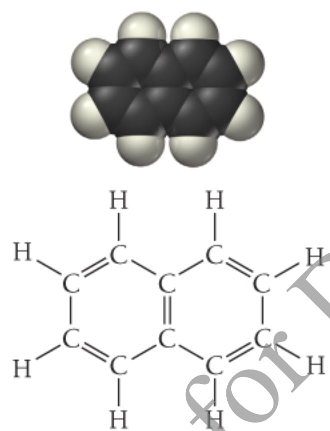
meta-dichlorobenzene or *m*-dichlorobenzene

para-dichlorobenzene or *p*-dichlorobenzene

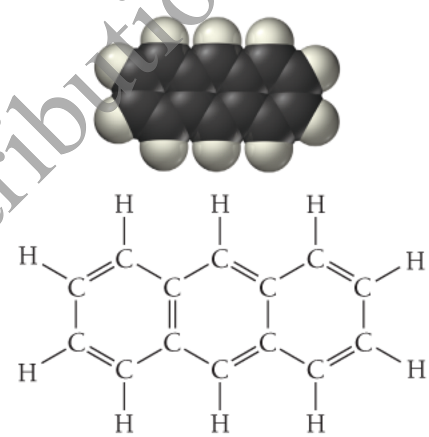
Compounds containing fused aromatic rings (rings with one or more shared sides) are called *polycyclic aromatic hydrocarbons*. Some common examples (shown in Figure 21.5) include naphthalene, the substance that composes mothballs, and pyrene, a carcinogen found in cigarette smoke.

Figure 21.5 **Polycyclic Aromatic Compounds**

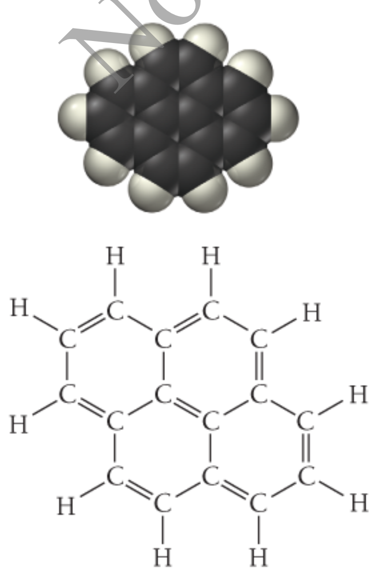
The structures of some common polycyclic aromatic compounds contain fused rings.



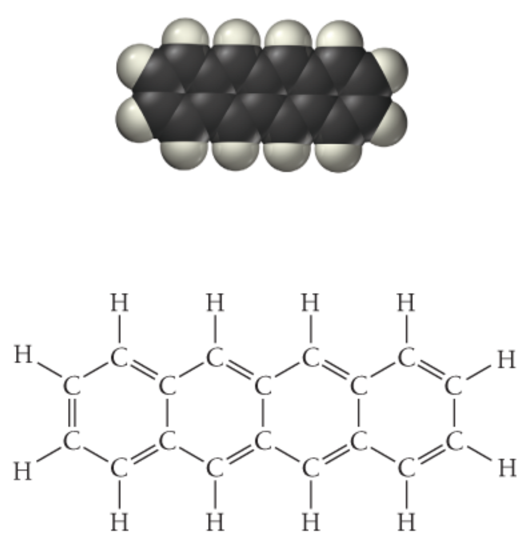
naphthalene



anthracene



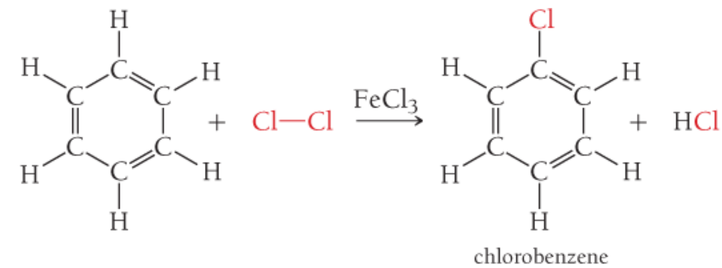
pyrene

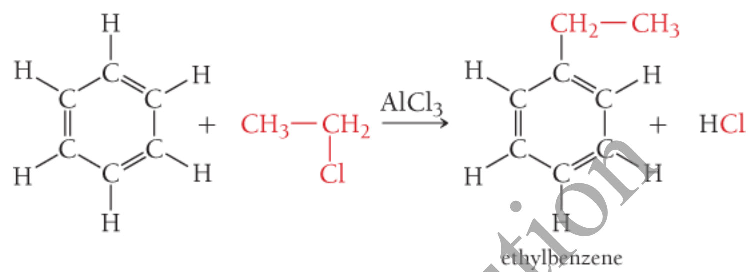


tetracene

Reactions of Aromatic Compounds

We might expect benzene to react similarly to the alkenes, readily undergoing addition reactions across its double bonds. However, because of electron delocalization around the ring and the resulting greater stability, benzene does not typically undergo addition reactions. Instead, benzene undergoes substitution reactions in which the hydrogen atoms are replaced by other atoms or groups of atoms as shown in these examples:





The substances shown over the arrows are catalysts needed to increase the rate of the reaction.