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880 CHAPTER 19 Amines

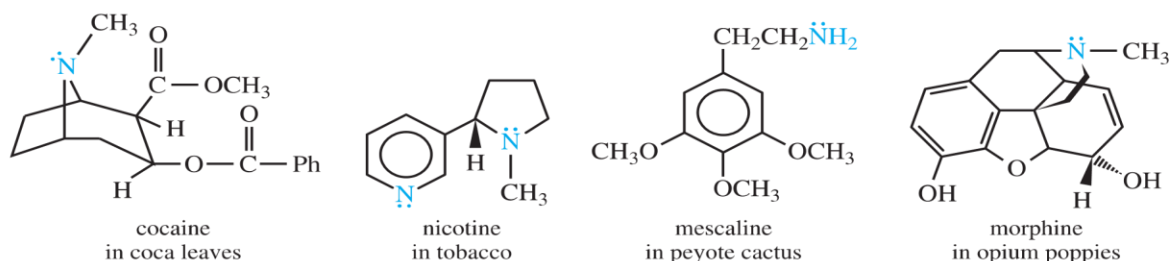
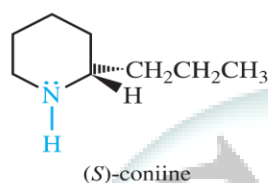


FIGURE 19-2
Some representative alkaloids.



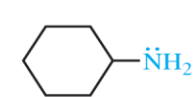
The *alkaloids* are an important group of biologically active amines, mostly synthesized by plants to protect them from being eaten by insects and other animals. The structures of some representative alkaloids are shown in Figure 19-2. Although some alkaloids are used medicinally (chiefly as painkillers), all alkaloids are toxic and cause death if taken in large quantities. The Greeks chose the alkaloid coniine to kill Socrates, although morphine, nicotine, or cocaine would have served equally well.

Mild cases of alkaloid poisoning can produce psychological effects that resemble peacefulness, euphoria, or hallucinations. People seeking these effects often become addicted to alkaloids. Alkaloid addiction frequently ends in death. Current estimates are over 400,000 deaths from alkaloid addiction in the United States per year, including both natural alkaloids like nicotine and cocaine, and synthetic alkaloids like methamphetamine. Most of these deaths result from addiction to nicotine in tobacco, a particularly difficult addiction to overcome.

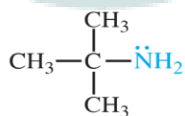
19-2
Nomenclature of Amines

Amines are classified as **primary** (1°), **secondary** (2°), or **tertiary** (3°), corresponding to one, two, or three alkyl or aryl groups bonded to nitrogen. In a heterocyclic amine, the nitrogen atom is part of an aliphatic or aromatic ring.

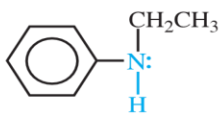
Primary (1°) amines



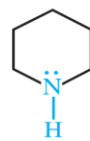
cyclohexylamine (1°)



tert-butylamine (1°)

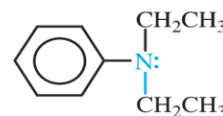


N-ethylaniline (2°)



piperidine (2°)

Tertiary (3°) amines

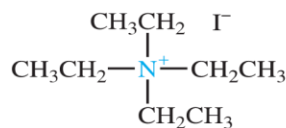


N,N-diethylaniline (3°)

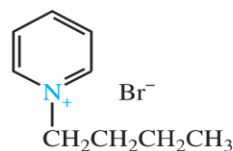


quinuclidine (3°)

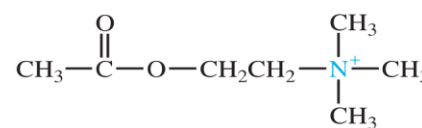
Quaternary ammonium salts have four alkyl or aryl bonds to a nitrogen atom. The nitrogen atom bears a positive charge, just as it does in simple ammonium salts such as ammonium chloride. The following are examples of quaternary (4°) ammonium salts:



tetraethylammonium iodide



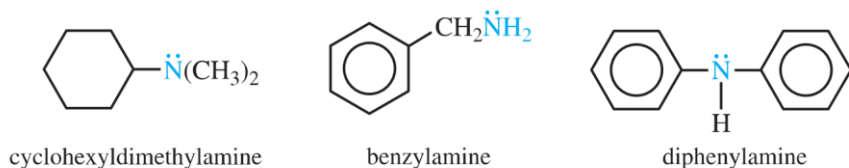
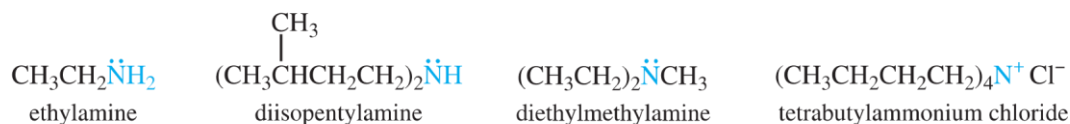
N-butylpyridinium bromide



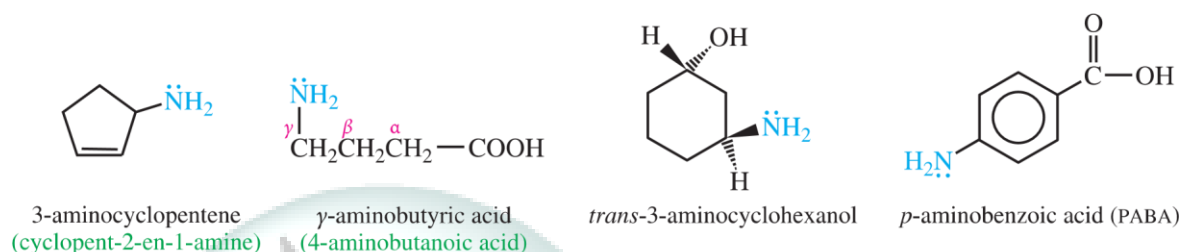
acetylcholine, a neurotransmitter

19-2A Common Names

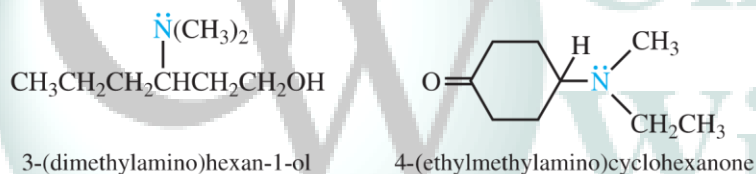
Common names of amines are formed from the names of the alkyl groups bonded to nitrogen, followed by the suffix *-amine*. The prefixes *di-*, *tri-*, and *tetra-* are used to describe two, three, or four identical substituents.



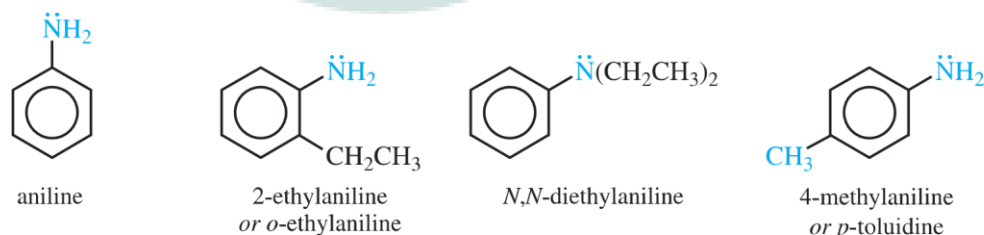
In naming amines with more complicated structures, the $-\text{NH}_2$ group is called the **amino** group. It is treated like any other substituent, with a number or other symbol indicating its position on the ring or carbon chain.



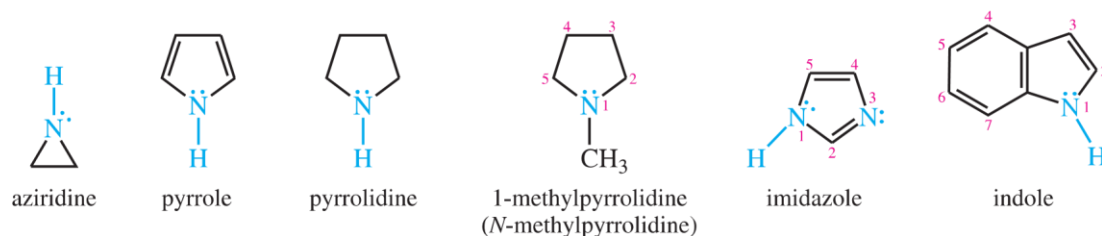
Using this system, secondary and tertiary amines are named by classifying the nitrogen atom (together with its alkyl groups) as an alkylamino group. The largest or most complicated alkyl group is taken to be the parent molecule.



Aromatic and heterocyclic amines are generally known by historical names. Phenylamine is called *aniline*, for example, and its derivatives are named as derivatives of aniline.

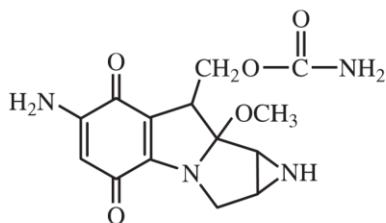


We first considered nitrogen heterocycles in Section 16-9. The names and structures of some common ones are shown here. The heteroatom is usually assigned position number 1.

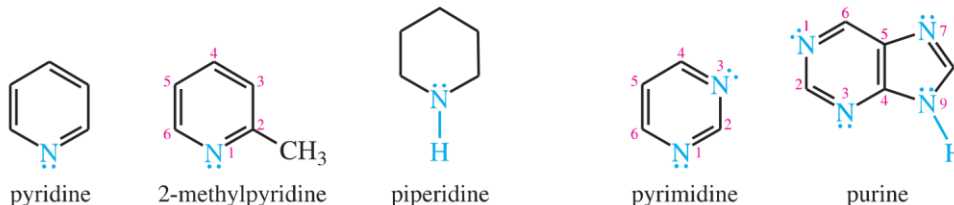


Application: Cancer Drug

Mitomycin C, an anticancer agent used to treat stomach and colon cancer, contains an aziridine ring. The aziridine functional group participates in the drug's degradation of DNA, resulting in the death of cancerous cells.



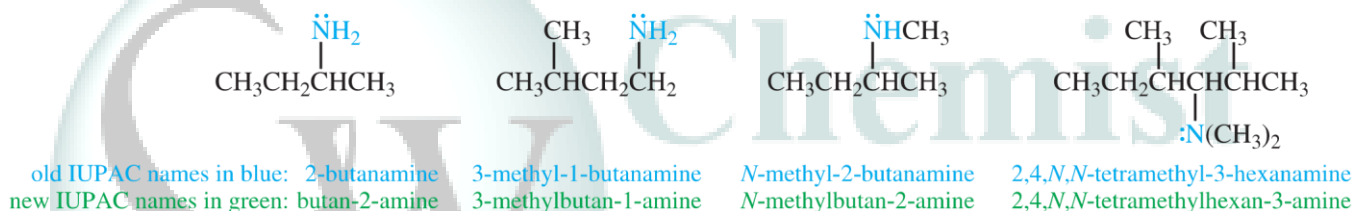
mitomycin C

**PROBLEM 19-1**

Determine which of the heterocyclic amines just shown are aromatic. Give the reasons for your conclusions.

19-2B IUPAC Names

The IUPAC nomenclature for amines is similar to that for alcohols. The longest continuous chain of carbon atoms determines the root name. The *-e* ending in the alkane name is changed to *-amine*, and a number shows the position of the amino group along the chain. Other substituents on the carbon chain are given numbers, and the prefix *N-* is used for each substituent on nitrogen.

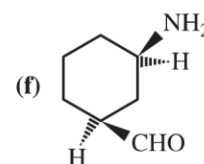
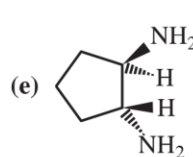
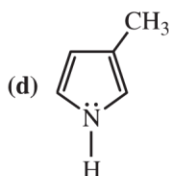
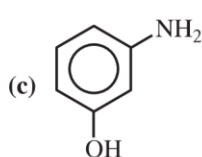
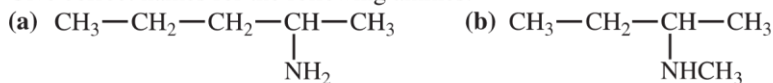
**PROBLEM 19-2**

Draw the structures of the following compounds:

- | | |
|--|------------------------------------|
| (a) <i>tert</i> -butylamine | (b) α -aminopropionaldehyde |
| (c) 4-(dimethylamino)pyridine | (d) 2-methylaziridine |
| (e) <i>N</i> -ethyl- <i>N</i> -methylhexan-3-amine | (f) <i>m</i> -chloroaniline |

PROBLEM 19-3

Give correct names for the following amines:



19-3 Structure of Amines

In Chapter 2, we saw that ammonia has a slightly distorted tetrahedral shape. A lone pair of nonbonding electrons occupies one of the tetrahedral positions. This geometry is represented by sp^3 hybridization of nitrogen, with the bulky lone pair compressing the H—N—H bond angles to 107° from the “ideal” sp^3 bond angle of 109.5° . Trimethylamine shows less angle compression because the bulky methyl groups open the angle slightly.