3.6: Amines - Structures and Names

Learning Objectives

- Identify the general structure for an amine.
- Determine the structural feature that classifies amines as primary, secondary, or tertiary.
- Generate common names of amines.
- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

An **amine** is an organic derivative of ammonia (NH_3) where one or more of the hydrogen atoms is replaced with a carbon group. Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A **primary (1°) amine** has one alkyl (or aryl) group on the nitrogen atom, a **secondary (2°) amine** has two, and a **tertiary (3°) amine** has three (Figure 3.6.1).

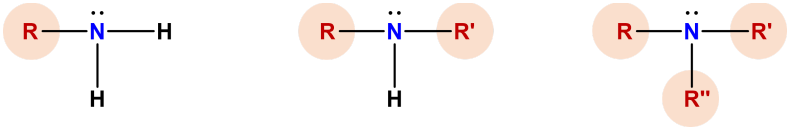


Figure 3.6.1: Structures of a primary (left), secondary (middle), and tertiary (right) amine.

Note

To classify alcohols, we look at the number of carbon atoms bonded to the *carbon atom* bearing the OH group, not the oxygen atom itself. Thus, although isopropylamine looks similar to isopropyl alcohol, the former is a *primary* amine, while the latter is a *secondary* alcohol.

Figure 3.6.2: Structures of isopropylamine (left) and isopropyl alcohol (right).

Physical Properties of Amines

Primary and secondary amines have hydrogen atoms bonded to an nitrogen atom and are therefore capable of hydrogen bonding (3.6.3*a*), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine (CH_3NH_2; −6°C) with those of ethane (CH_3CH_3; −89°C) and methanol (CH_3OH; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table 3.6.1).

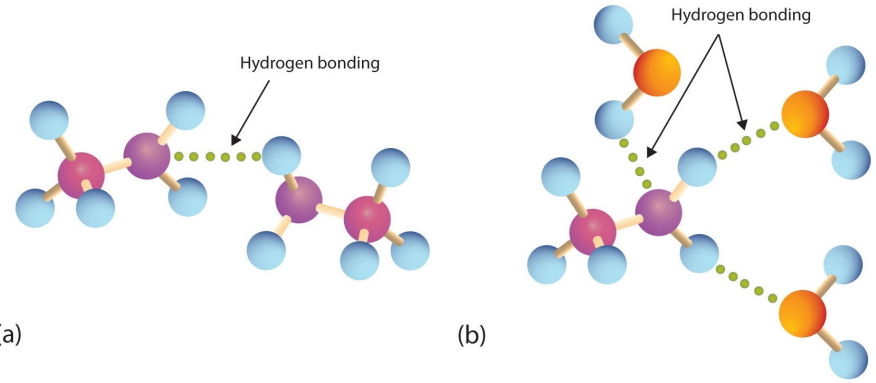


Figure 3.6.3: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

Table 3.6.1. Comparison of properties of amines and oxygen-containing molecules.

Name	Condensed Structure	Classification	Molar Mass (g/mol)	Boiling Point (°C)	Solubility at 25 °C (g/100 g water)
butylamine	$CH_3CH_2CH_2CH_2NH_2$	1°	73	78	miscible
diethylamine	$(CH_3CH_2)_2NH$	2°	73	55	miscible
butyl alcohol	$CH_3CH_2CH_2CH_2OH$	—	74	118	8
dipropylamine	$(CH_3CH_2CH_2)_2NH$	2°	101	111	4
triethylamine	$(CH_3CH_2)_3N$	3°	101	90	14
dipropyl ether	$(CH_3CH_2CH_2)_2O$	—	102	91	0.25

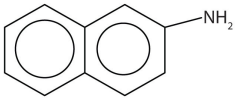
All three classes of amines can engage in hydrogen bonding with water (Figure 3.6.3*b*). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.

$$HOCH_2CH_2OH$$

Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.



Naming Amines

The common names for simple aliphatic amines consist of an alphabetic list of alkyl groups attached to the nitrogen atom, followed by the suffix ***-amine***. The amino group (NH_2) is named as a substituent in more complicated amines, such as those that incorporate other functional groups or in which the alkyl groups cannot be simply named.

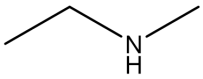


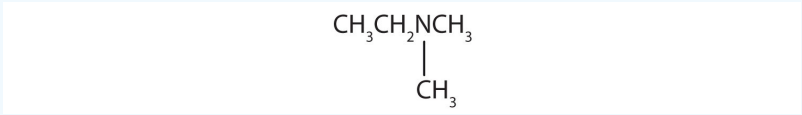
Figure 3.6.4: Structure of a simple amine.

Determining the classification of an amine can help with identifying the common name. Since the above amine has two carbon groups attached to the nitrogen, it represents a secondary amine. This indicates that two carbon groups should be identified and included in the common name. The group to the left of the nitrogen represents an ethyl group and the group to the right is a methyl group. Therefore, the common name of the amine shown in Figure 3.6.4 is *ethylmethylamine*.

Example 3.6.1

Name and classify each compound.

a. $CH_3CH_2CH_2NH_2$

b. 

c. $CH_3CH_2NHCH_2CH_3$

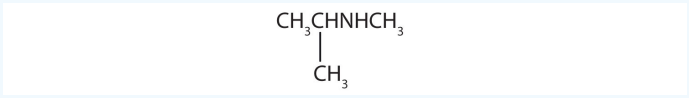
d. $CH_3CH_2CH_2NHCH_3$

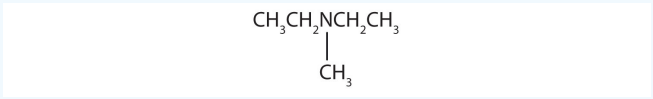
Solution

a. There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is propylamine.
b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is ethyldimethylamine, a tertiary amine.
c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is diethylamine.
d. The nitrogen atom has a methyl group and a propyl group, so the compound is methylpropylamine, a secondary amine.

Exercise 3.6.1

Name and classify each compound.

a. 

b. 

c. $CH_3CH_2CH_2CH_2NH_2$

d. $CH_3CH_2CH_2NHCH_2CH_2\ CH_3$

Example 3.6.2

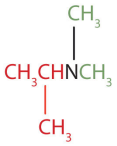
Draw the structure for each compound and classify.

a. isopropyldimethylamine

b. dipropylamine

Solution

a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.



b. The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) $CH_3CH_2CH_2NHCH_2CH_2CH_3$

? Exercise 3.6.2

Draw the structure for each compound and classify.

a. ethylisopropylamine
b. diethylpropylamine

The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—**aniline**. Aryl amines are named as derivatives of aniline.

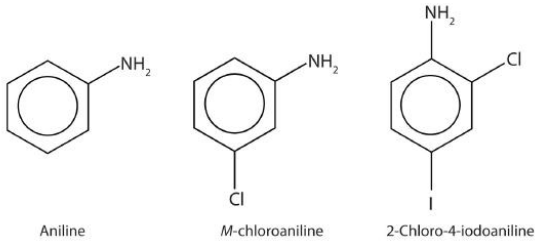
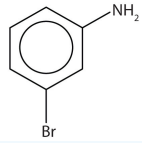


Figure 3.6.5 Structure of anlinine (left) and its derivatives.

✓ Example 3.6.3

Name this compound.

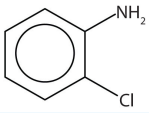


Solution

The benzene ring with an amino (NH_2) group is aniline. The compound is named as a derivative of aniline: 3-bromoaniline or *m*-bromoaniline.

? Exercise 3.6.3

Name this compound.

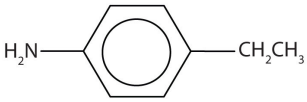


✓ Example 3.6.4

Draw the structure for *p*-ethylaniline and classify.

Solution

The compound is a derivative of aniline. It is a primary amine having an ethyl group located *para* to the amino (NH_2) group.



Exercise 3.6.4

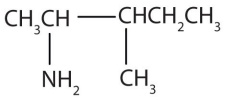
Draw the structure for *p*-isopropylaniline and classify.

Example 3.6.5

Draw the structure for 2-amino-3-methylpentane.

Solution

Always start with the parent compound: draw the pentane chain. Then attach a methyl group at the third carbon atom and an amino group at the second carbon atom.



Exercise 3.6.5

Draw the structure for 2-amino-3-ethyl-1-chloroheptane.

Chemical Behavior of Amines

Amines behave as weak Brønsted-Lowry bases in water. These weak bases gain protons from water to form a **protonated amine** (Figure 3.6.6).

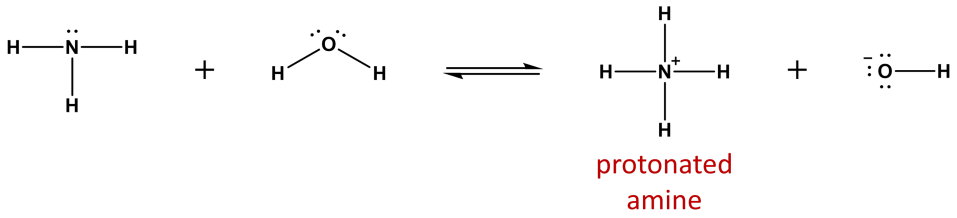


Figure 3.6.6: Acid-base reaction where the amine gains a proton from water to form a protonated amine.

When an amine is neutralized by an acid, an **amine salt** is produced (Figure 3.6.7).

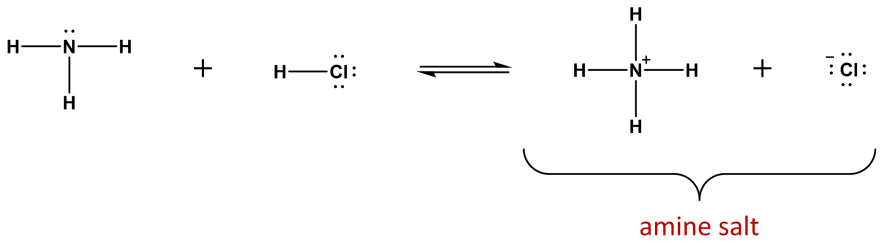


Figure 3.6.7: Acid-base reaction where the amine gains a proton from a strong acid to form an amine salt.

Ammonium (NH_4^+) ions, in which one or more hydrogen atoms are replaced with alkyl groups, are named in a manner analogous to that used for simple amines. The alkyl groups are named as substituents, and the parent species is regarded as the NH_4^+ ion. For example, $CH_3NH_3^+$ is the methylammonium ion. The ion formed from aniline ($C_6H_5NH_3^+$) is called the anilinium ion.

Example 3.6.6

Name each ion.

a. $CH_3NH_3^+$
b. $(CH_3)_2NH_2^+$
c. $(CH_3)_3NH^+$
d. $(CH_3)_4N^+$

Solution

The ions have one, two, three, and four methyl (CH_3) groups attached to a nitrogen atom. Their names are as follows:

a. methylammonium ion
b. dimethylammonium ion
c. trimethylammonium ion
d. tetramethylammonium ion

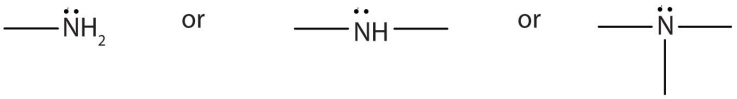
Exercise 3.6.6

Name each ion.

a. $CH_3CH_2NH_3^+$
b. $(CH_3CH_2)_3NH^+$
c. $(CH_3CH_2CH_2)_2NH_2^+$
d. $(CH_3CH_2CH_2CH_2)_4N^+$

Summary

- An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. Amines are classified as primary, secondary, or tertiary based on the number of hydrocarbon groups attached to the nitrogen atom. The amine functional group is as follows:



- Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.