1.7 Amines and Amides

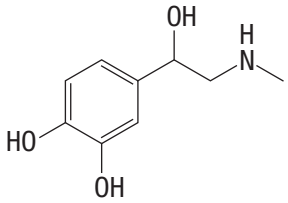
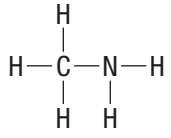


Figure 1 The epinephrine (adrenaline) molecule. The –NH group on the right of the molecule is bonded to 2 carbon atoms, making this compound a secondary amine.

Figure 2 Epinephrine auto-injection syringes can be lifesavers for people who are susceptible to severe allergic reactions.

amine an organic compound, related to ammonia, that contains a nitrogen atom bonded to one or more alkyl groups on each molecule



methanamine

Figure 3 Alternative names for methanamine are methylamine and aminomethane.

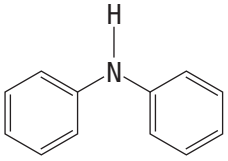
During a severe allergic reaction, the body's immune system overreacts to the presence of a foreign substance. The allergic reaction causes the tissues of the airway to swell and the lungs to fill with fluid. If not treated quickly, this severe reaction can cause death. The most common treatment for severe allergic reactions is epinephrine, also known as adrenaline. Epinephrine is a hormone produced naturally by the adrenal glands. The hormone molecules contain a functional group called an amino group, –NH (**Figure 1**). Most people who have severe allergies to common substances, such as bee venom or peanuts, carry auto-injection syringes filled with epinephrine with them at all times (**Figure 2**). Amines are one class of organic compounds that contain nitrogen.

Amines

An **amine** is a derivative of ammonia in which one or more of the hydrogen atoms are replaced with alkyl groups. Amines are classified as primary (1°) if one alkyl group is attached to the nitrogen atom, secondary (2°) if two alkyl groups are present, and tertiary (3°) if all three hydrogen atoms in ammonia have been replaced by alkyl groups. **Table 1** lists some common amines.

Amines generally have strong, often unpleasant, odours, sometimes described as "fishy." Many amine odours resemble ammonia. For example, urine contains amines that come from the breakdown of proteins. The odours associated with decaying animal and human tissues are caused by amines such as putrescine, $H_2N(CH_2)_4NH_2$, and cadaverine, $H_2N(CH_2)_5NH_2$. Notice that these compounds have an amino group at either end of each molecule. Aromatic amines are used to make dyes. Since many of them are carcinogenic, they must be handled with great care. CAREER LINK

Table 1 Some Common Amines

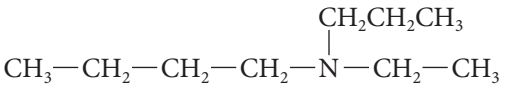
Formula	Systematic IUPAC name	Common name	Type
CH_3NH_2	methanamine	methylamine	primary
$CH_3CH_2NH_2$	ethanamine	ethylamine	primary
$(CH_3)_2NH$	*N*-methylmethanamine	dimethylamine	secondary
$(CH_3)_3N$	*N*,*N*-dimethylmethanamine	trimethylamine	tertiary
$C_6H_5NH_2$	aniline	aniline	primary
	*N*-phenylaniline	diphenylamine	secondary

Naming Amines

Consider the primary amine with the structure CH_3NH_2. Using the IUPAC naming system, this molecule would be named by adding the *-amine* suffix to the name of the chain or ring to which it is attached. The *-e* is removed from this name, giving the name methanamine (**Figure 3**).

Note that, in Table 1, the IUPAC name for an aromatic amine consisting of an amine group attached to a benzene ring is aniline, rather than benzamine.

To name secondary and tertiary amines, begin with an amine name based on the name of the longest alkyl group. We use the locator, *N*, to indicate the attachment of additional chains to the nitrogen atom, just as we use a number to indicate a specific carbon atom. For example, an amine with an ethyl group, a propyl group, and a butyl group, each bonded to the nitrogen atom at carbon number 1, is named *N*-ethyl-*N*-propylbutan-1-amine.



N-ethyl-*N*-propylbutan-1-amine

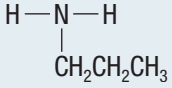
As you have already read, some compounds contain more than one amino group. A molecule of cadaverine, for example, is a 5-carbon chain with an amino group at each end: $NH_2(CH_2)_5NH_2$. This type of compound is called a diamine, so cadaverine's IUPAC name is pentane-1,5-diamine.

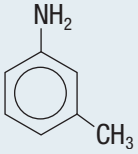
Tutorial 1 Naming and Drawing Amines

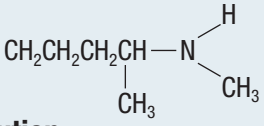
This tutorial will give you practice in drawing and naming amines.

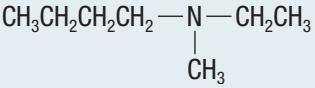
Sample Problem 1: Naming Amines from Their Structures

Name each of the following amines according to the IUPAC system:

(a) 

(c) 

(b) 

(d) 

Solution

(a) The longest carbon chain is a propyl group, whose terminal carbon atom is bonded to the nitrogen atom. This is the only alkyl group attached to the nitrogen atom, so the compound is a primary amine. The compound's name is propan-1-amine.

(b) This compound is a secondary amine with a pentyl group attached at its second carbon atom and a methyl group. The amine's name is based on the longer group: the pentyl group. The name of the compound is *N*-methylpentan-2-amine.

(c) The root name for an amine attached to a benzene ring is aniline. There is also a substituent methyl group on the third carbon atom. The name of the compound is 3-methylaniline.

(d) This is a tertiary amine whose longest carbon chain has 4 carbon atoms: butanamine. The two substituents are a methyl group and an ethyl group. The compound is named *N*-ethyl-*N*-methylbutan-1-amine.

Sample Problem 2: Drawing Amines

Draw the structural formula and write the name of each of the following amines, with ethyl as the attached alkyl group(s):

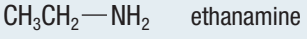
(a) a primary amine

(b) a secondary amine

(c) a tertiary amine

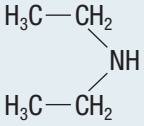
Solution

(a) A primary amine has one alkyl group attached to the nitrogen atom.



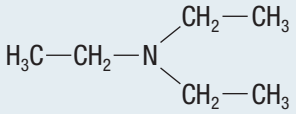
ethanamine

(b) A secondary amine has two alkyl groups and one hydrogen atom bonded to the nitrogen atom.



N-ethylethanamine

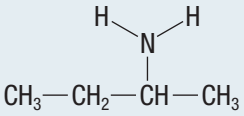
(c) A tertiary amine has three alkyl groups but no hydrogen atoms bonded to the nitrogen atom.

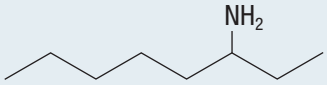


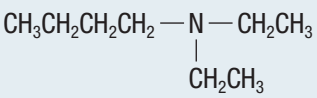
N,N-diethylethanamine

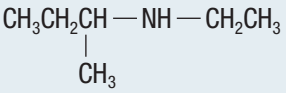
Practice

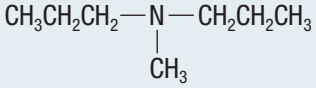
1. Name each of the following compounds: K/U

(a) 

(d) 

(b) 

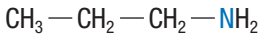
(e) 

(c) 

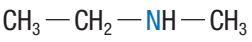
2. Draw the structure of each of the following compounds: K/U C
   (a) 2-methylpropan-1-amine
   (b) a primary amine with a 2-carbon alkyl group

Properties of Amines

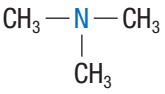
Small amines are soluble in water. Since nitrogen is more electronegative than either carbon or hydrogen, the N−C bonds and any N−H bonds are polar. This polarity increases the strength of the van der Waals forces between molecules so more energy is needed to separate them. That means that amines have higher melting points and higher boiling points than corresponding hydrocarbon compounds. The series of amines in **Figure 4** explains the effect that reducing the number of −NH groups has on the boiling points of amines of similar size.

(a) 

primary amine
b.p. 49 °C

(b) 

secondary amine
b.p. 37 °C

(c) 

tertiary amine
b.p. 3 °C

Figure 4 Boiling points (b.p.) for three possible CH isomers of an amine, each with 3 carbon atoms. The primary amine, (a), can form two hydrogen bonds and hence has the highest boiling point. The tertiary amine, (c), cannot form hydrogen bonds at all and hence has the lowest boiling point.

Amides

Amides are structurally similar to esters, except the two chains are joined by a nitrogen atom next to a carbonyl group rather than by an oxygen atom (**Figure 5**). The amide functional group consists of a carbonyl group bonded to a nitrogen atom.

amide an organic compound that contains a carbonyl group bonded to a nitrogen atom

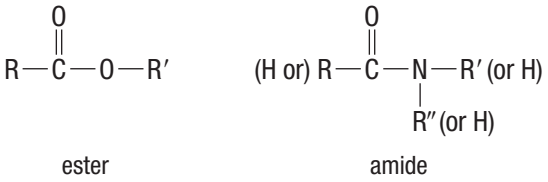


Figure 5 General structures of esters and amides illustrate that the compounds include one or more alkyl groups. These groups, which might be the same or different, are represented in the diagrams by the symbols R, R′, and R″.

Carboxylic acids react with alcohols to produce esters. Carboxylic acids react in a similar way with ammonia, primary amines, and secondary amines to produce amides. You will learn more about these reactions a little later in this section.

Naming Amides

Naming amides is similar to naming esters. The name of an amide has three parts: the first part from the amine; the second part from the acid; and the ending, which is always the suffix *-amide*. For example, the reaction of methanamine and butanoic acid will produce an amide: *N*-methylbutanamide (**Figure 6**).

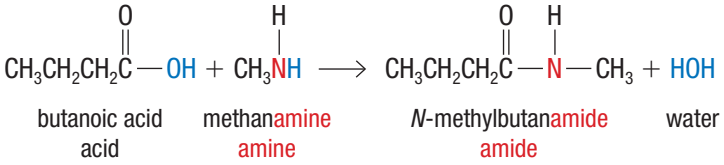


Figure 6 Note how to derive the name of the amide from the names of the amine and the carboxylic acid.

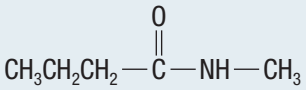
Tutorial 2 Naming and Drawing Amides

This tutorial will give you practice in naming and drawing amides.

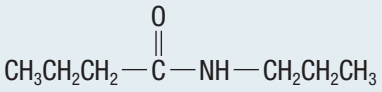
Sample Problem 1: Naming Amides from Their Structures

Name each of the following amides:

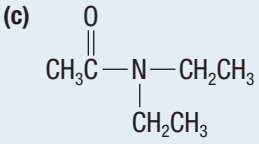
(a)



(b)



(c)



Solution (a)

The first part of the compound came from a carboxylic acid, with 4 carbon atoms: butanoic acid. The second part of the compound came from a primary amine with 1 carbon atom: methanamine. The name of the amide is *N*-methylbutanamide.

Solution (b)

The carboxylic acid had a chain with 4 carbon atoms: butanoic acid. The amine was a primary amine with 3 carbon atoms: propanamine. The name of the amide is *N*-propylbutanamide.

Solution (c)

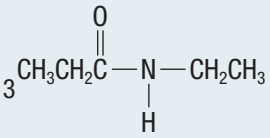
The carboxylic acid had 2 carbon atoms: ethanoic acid. The amine was a secondary amine: *N*-ethylethanamine. The name of the amide is *N,N*-diethylethanamide.

Sample Problem 2: Drawing Amides

Draw the structure of *N*-ethylpropanamide.

Solution

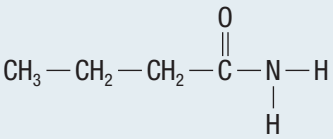
The alkyl group bonded to the nitrogen atom (from the amine) is ethyl. It therefore has 2 carbon atoms. The carbonyl group from the carboxylic acid is attached to a propan- chain, so has 3 carbon atoms. Therefore, the structure is as shown at right:



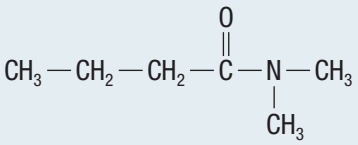
Practice

1. Name each of the following amides: K/U

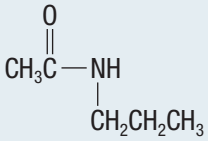
(a)



(c)



(b)



2. Draw the structure of each of the following amides: K/U C

(a) *N,N*-diethylethanamide (b) *N*-methylbutanamide

Investigation 1.7.1

Building Organic Molecular Models (page 69)

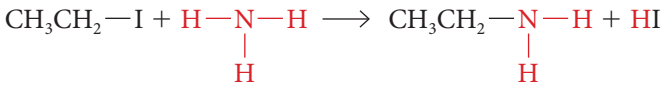
This investigation gives you an opportunity to put into practice your knowledge of the names and properties of amines and amides. You will have the opportunity to build and explore models of these compounds.

Properties of Amides

The smaller amides are somewhat soluble in water. This can be explained by the molecules' structure: the –NH groups form hydrogen bonds with water molecules. As the length of the carbon chain increases, solubility decreases. Primary amides, with their nitrogen atoms each bonded to 2 hydrogen atoms, have higher melting points and boiling points than similar amides. This is likely due to more hydrogen bonding between primary amide molecules.

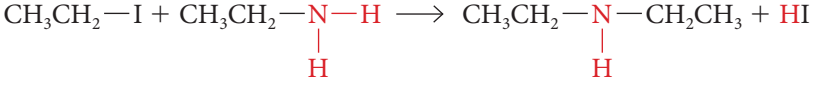
Reactions Involving Amines and Amides

An amine can generally be synthesized from an alkyl halide and ammonia. For example,



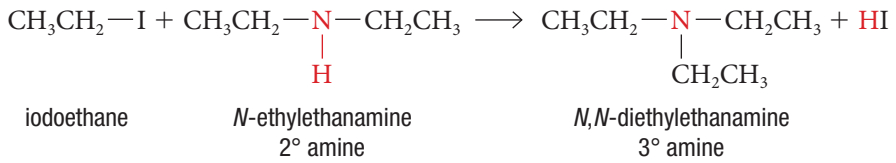
iodoethane ammonia ethanamine, 1° amine

Ethanamine is a primary amine. It reacts with additional iodoethane to form a secondary amine, *N*-ethylethanamine, and hydrogen iodide:



iodoethane ethanamine, 1° amine *N*-ethylethanamine, 2° amine

N-ethylethanamine also reacts with iodoethane, this time forming a tertiary amine, *N,N*-diethylethanamine, along with hydrogen iodide.



Amides can be synthesized by the condensation reaction of a carboxylic acid with ammonia or primary or secondary amines (**Figure 7**).

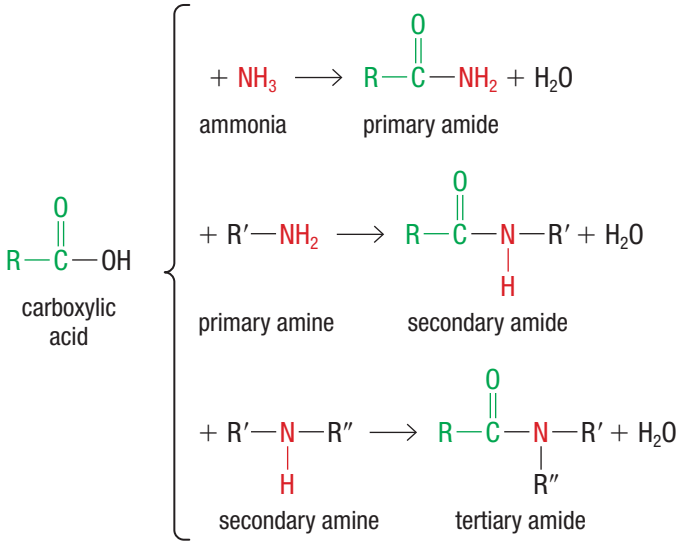


Figure 7 The structure of the amide product depends on whether the carboxylic acid reacts with ammonia, a primary amine, or a secondary amine.

An example of the synthesis of an amide is the reaction of butanoic acid with methanamine to produce *N*-methylbutanamide plus water.

The reactions above are reversible: Amides can be hydrolyzed in acidic or basic conditions to produce the carboxylic acid and the amine.

1.7 Review

Summary

- Amines can be viewed as alkyl groups bonded to a nitrogen atom or an amino group bonded to an alkane. Primary amines have one alkyl group attached to the nitrogen atom; secondary amines have two; tertiary amines have three.
- Amines are named by adding the suffix *-amine* to the root of the name of the longest alkyl group attached to the nitrogen atom. The prefix *N-* indicates that a second (and third) alkyl group is also attached to the nitrogen atom.
- Amides are formed from the reaction of carboxylic acid and amines. Amides can be hydrolyzed to re-form the amine and carboxylic acid.
- Amides are named with the root of the name of the carboxylic acid first, followed by the root of the name of the amine, and ending with *-amide*.

Questions

1. Name each of the following compounds: K/U

(a) $CH_3CH_2C(=O)-NH_2$

(b) $CH_3CH_2CH_2-N(-CH_3)-CH_3$

(c) $CH_3CH_2C(=O)-N(-CH_2CH_3)-CH_2CH_3$

(d) $CH_3CH(Cl)CH_2CH(NH_2)CH_2CH_2CH_3$

(e) $CH_3CH(NH_2)CH_2CH(NH_2)CH_2CH=CH_2$

2. Copy and complete **Table 2** in your notebook. K/U C

3. Draw the structural formulas for the isomers of C_3H_9N. Show at least one primary, one secondary, and one tertiary amine. K/U C

4. Write a structural formula equation that represents the formation of *N*,*N*-diethylpropanamide. K/U

5. Identify the reaction type and write the structures and names for the products you would expect for each of the following reactions: K/U C

(a) $H_3C-CH_2-Br + H_3N-CH_2-CH_3$

(b) $H_3C-CH_2-Br + H_3C-NH-CH_2-CH_3$

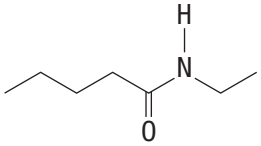
(c) ethanoic acid and propan-1-amine

6. Create a flow chart showing how you would synthesize *N*,*N*-dimethylethanamide from an alkane, an alkene, a halogen, and ammonia. Draw and name each compound. T/I C

7. Several amines are used in natural gas processing. Research how these amines reduce air pollution. Create a storyboard or diagram to communicate your findings. T/I C A

WEB LINK

Table 2

Name	Condensed structure	Line diagram or structural formula	Type of compound
N,*N*-dimethylbutanamide			
	$CH_3CH_2CH_2NH_2$		
			
	$CH_3CH_2CH_2CH_2CH_2NHCH_3$		
N-methylbutan-1-amine