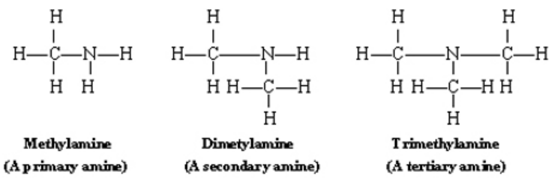
8.19: Organic Nitrogen Compounds

There is a tremendous variety of organic compounds which can be derived from carbon, hydrogen, and oxygen which is evident from the numerous previous sections discussing these compounds. If we include nitrogen as a possible constituent of these molecular structures, many more possibilities arise. Most of the nitrogen-containing compounds are less important commercially, however, and we will only discuss a few of them here.

Amines may be derived from ammonia by replacing one, two, or all three hydrogens with alkyl groups. Some examples are



Structures of methylamine, dimethylamine, and trimethylamine which is a primary amine, secondary amine, and tertiary amine respectively.

The terms primary (one), secondary (two), and tertiary (three) refer to the number of hydrogens that have been replaced. Both primary and secondary amines are capable of hydrogen bonding with themselves, but tertiary amines have no hydrogens on the electronegative nitrogen atom.

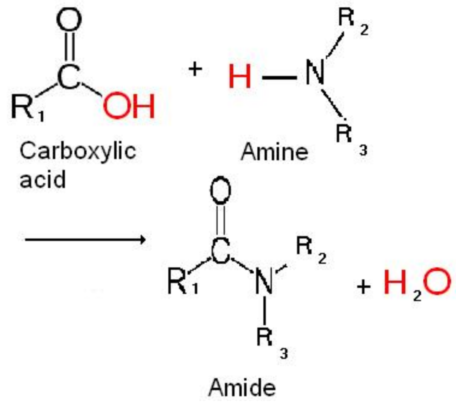
Amines usually have unpleasant odors, smelling “fishy“. The three methylamines listed above can all be isolated from herring brine. Amines, as well as ammonia, are produced by decomposition of nitrogen-containing compounds when a living organism dies. The methylamines are obtained commercially by condensation of methanol with ammonia over an aluminum oxide catalyst:

$$CH_3OH + NH_3 \xrightarrow[Al_2O_3]{400^\circ C} CH_3NH_2 + H_2O$$
$$CH_3OH + CH_3NH_2 \xrightarrow[Al_2O_3]{400^\circ C} (CH_3)_2NH + H_2O$$
$$CH_3OH + (CH_3)_2NH \xrightarrow[Al_2O_3]{400^\circ C} (CH_3)_3N + H_2O$$

First equation shows methanol reacting with ammonia to give methylamine and water. Next equation shows methanol reacting with methylamine to give dimethylamine and water. Final equation shows methanol reacting with dimethylamine to give tri-methylamine and water.

Dimethylamine is the most important, being used in the preparation of herbicides, in rubber vulcanization, and to synthesize dimethylformamide, an important solvent.

Amides are another important nitrogen containing organic compound. The key feature of an amine is a nitrogen atom bonded to a carbonyl carbon atom. Like esters, amides are formed in a condensation reaction. While esters are formed from the condensation reaction of an alcohol and a carboxylic acid, amides are formed from the condensation of an amine and a carboxylic acid:

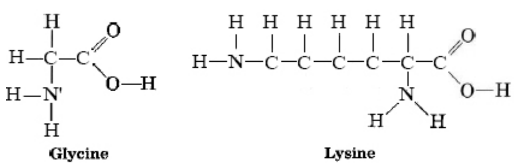


General equation for amide condensation is shown with the reaction of a carboxylic acid and an amine to give amide and water.

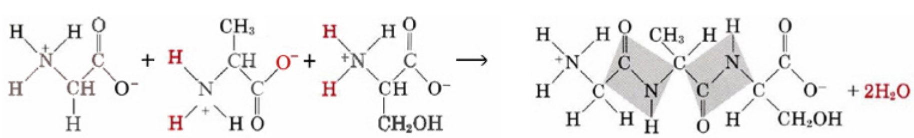
This general reaction is usually unfavorable, because the hydroxyl group acts as a bad leaving group. Organic chemists have devised methods to work around this by using certain chemicals to activate the carboxylic acid and allow for the addition of the amine.

As amides are formed by condensation reactions, many important condensation polymers involve amide linkages. Nylon, for instance, is formed from the amide condensation of hexamethylenediamine and adipic acid.

A second set of condensation polymers formed from amide linkages are the proteins and peptides found in your body and in all organisms. These polymers are formed from another organic nitrogen compound, the **amino acid.** These molecules contain both an amine group and a carboxyl group. Examples of such **amino acids** are glycine and lysine:



Amino acids are the constituents from which proteins are made. Some, like glycine, can be synthesized in the human body, but others cannot. Lysine is an example of an **essential amino acid**—one which must be present in the human diet because it cannot be synthesized within the body. As mentioned, the condensation of amino acids into peptides forms amide linkages. For this reason, scientists sometimes refer to the *amide backbone* of a protein or peptide. A protein has a long series of amide bonds, as can be seen in the following figure showing the synthesis of a tri-peptide from three amino acids:



Equation shows the removal of 2 moles of water from the formation of a tri-peptide from three amino acids.

Amino acids and proteins further discussed in the sections on enzymes and in a set of sections devoted to proteins and their chemistry in living systems.

The intermolecular forces and boiling points of nitrogen-containing organic compounds may be explained according to the same principles used for oxygen-containing substances.

Example 8.19.1: Boiling Points

Rationalize the following boiling points: (a) 0°C for $CH_3CH_2CH_2CH_3$; (b) 11°C for $CH_3CH_2OCH_3$; (c) 97°C for $CH_3CH_2CH_2OH$; and (d) 170°C for $NH_2CH_2CH_2OH$.

Solution All four molecules have very similar geometries and the same number of electrons (26 valence electrons plus 8 core electrons), and so their London forces should be about the same. Compound (a) is an alkane and is nonpolar. By contrast compound (b) is an ether and should be slightly polar. This slight polarity results in a slightly higher boiling point. Compound

(c) is isomeric with compound (b) but is an alcohol. There is hydrogen bonding between molecules of (c), and its boiling point is much higher. Molecule (d) has both an amino group and a hydroxyl group, each of which can participate in hydrogen bonding. Consequently it has the highest boiling point of all.