

Chapter 24 – Amines and Heterocycles

Chapter Outline

- I. Facts about amines (Section 24.1–24.5).
 - A. Naming amines (Section 24.1).
 1. Amines are classified as primary (RNH_2), secondary (R_2NH), tertiary (R_3N) or quaternary ammonium salts (R_4N^+).
 2. Primary amines are named in several ways:
 - a. For simple amines, the suffix *-amine* is added to the name of the alkyl substituent.
 - b. The suffix *-amine* can replace the final *-e* of the parent compound.
 - c. For more complicated amines, the $-\text{NH}_2$ group is an amino substituent on the parent molecule.
 3. Secondary and tertiary amines:
 - a. Symmetrical amines are named by using the prefixes *di-* and *tri-* before the name of the alkyl group.
 - b. Unsymmetrical amines are named as *N*-substituted primary amines.
 - i. The largest group is the parent.
 4. The simplest arylamine is aniline.
 5. Heterocyclic amines (nitrogen is part of a ring) have specific parent names.
 - a. The nitrogens receive the lowest possible numbers.
 - B. Structure and properties of amines (Section 24.2).
 1. The three amine bonds and the lone pair occupy the corners of a tetrahedron.
 2. An amine with three different substituents is chiral.
 - a. The two amine enantiomers interconvert by pyramidal inversion.
 - b. This process is rapid at room temperature.
 3. Amines with fewer than 5 carbons are water-soluble and form hydrogen bonds.
 4. Amines have higher boiling points than alkanes of similar molecular weight.
 5. Amines smell nasty!
 - C. Basicity of amines (Sections 24.3–24.5).
 1. The lone pair of electrons makes amines both nucleophilic and basic (Section 24.3).
 2. The basicity constant K_b is the measure of the equilibrium of an amine with water.
 - a. The larger the value of K_b (smaller $\text{p}K_b$), the stronger the base.
 3. More often, K_a is used to describe amine basicity.
 - a. K_a is the dissociation constant of the conjugate acid of an amine.
 - b. $\text{p}K_a + \text{p}K_b = 14$ (for aqueous media).
 - c. The smaller the value of K_a (larger $\text{p}K_a$), the stronger the base.
 4. Base strength.
 - a. Primary, secondary, and tertiary alkylamines have similar basicities.
 - b. Arylamines and heterocyclic amines are less basic than alkylamines.
 - i. The sp^2 electrons of the pyridine lone pair are less available for bonding.
 - ii. The pyrrole lone pair electrons are part of the aromatic ring π system.
 - c. Amides are nonbasic.
 - d. Amine basicity can be used as a means of separating amines from a mixture.
 - i. An amine can be converted to its salt, extracted from an organic solution with water, neutralized, and re-extracted with an organic solvent.
 - e. Some amines are very weak acids.
 - i. LDA is formed from diisopropylamine and acts as a strong base.

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