

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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