

## 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 ( $\text{RNH}_2$ ), secondary ( $\text{R}_2\text{NH}$ ), tertiary ( $\text{R}_3\text{N}$ ) or quaternary ammonium salts ( $\text{R}_4\text{N}^+$ ).
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  $\pi$  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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