

Chapter 15

Amines

Amines have single bonds of Carbon bound to Nitrogen. Many of the molecules that carry chemical messages (such as neurotransmitters) are amines. They are present in many kinds of essential biomolecules and pharmaceutical agents!

Amines contain one or more organic groups bonded to nitrogen...the compounds have these general formulas:



Amines are organic derivatives of ammonia and are classified as primary, secondary and tertiary, depending on the number of organic groups bound directly to the Nitrogen atom.

Each amine nitrogen has a lone pair of electrons. The lone pair is not always written, but it is ALWAYS THERE! It is responsible in large part for the chemistry of amines. When a fourth group bonds through the lone pair, the product is a quaternary ammonium ion, which has a positive charge and forms ionic compounds with anions...for example....

The groups bonded to the amine nitrogen atom may be -alkyl or -aryl groups (aryl refers to a benzene ring) and may or may not contain other functional groups. For example...

Naming primary alkyl amines

- Identify the alkyl group attached to nitrogen
- Add the suffix *-amine* to the alkyl group name

Naming simple, nonheterocyclic secondary and tertiary amines

- Add the appropriate prefix *-di*, *-tri* to alkyl group name
- Use suffix *-amine*

Naming tertiary amines with varying R groups

- Name the compound as N-substituted derivatives of a primary amine
- The parent is the primary amine that contains the largest of the R groups
- All other groups are considered to be N-substituents (they are attached directly to the Nitrogen)

Naming heterocyclic amines

- Nitrogen is part of ring structure
- Nomenclature too difficult to deal with
- Simplest one is aniline

When to use *-amino* prefix

- Use this prefix in cases where there are higher-priority groups present
 - Alcohols, carboxylic acid derivatives are main ones

15.2 Properties of Amines

The lone electron pair on the Nitrogen causes amines to be LEWIS BASES by forming a bond with a H^+ ion from an acid or a water.

Primary and Secondary: Unshared electron pair can H-bond to H atoms from water or other primary and secondary amines. This means they have higher boiling points (but not as high as alcohols)

Tertiary: Cannot H-bond with each other
Have much lower BP than alcohols and primary/secondary amines

All: Can H-bond to water through the lone electron pair. This means that amines up to 6 Carbons are soluble in water.

- Many amines cause physiological problems/responses
- Simpler amines are irritating and toxic
- Some complex amines from plants are poisonous
- Many useful drugs are amines
- Many have strong odors (some smell like ammonia, others smell like dead fish or rotten meat)

15.3 Heterocyclic Nitrogen Compounds

In many nitrogen-containing compounds, the nitrogen is part of a ring or benzene ring. These are the heterocycles...both nonaromatic and aromatic.

15.4 Basicity of Amines

Amines are weak bases and very rarely behave as acids. If you place an amine in water, it forms an ammonium ion:

Note that this is a reversible reaction...in the reverse reaction ammonium ions can react as acids in the presence of bases to regenerate the amine:

Ammonium ions are also formed in the reactions of amines with the hydronium ion in acidic solutions:

The positive ions formed here are named by replacing the ending *-amine* with the ending *-ammonium*. To name the ions of heterocyclic amines, the amine name is modified by replacing the *-e* with *-ium*:

As a result of the equilibrium, amines exist as ammonium ions in the aqueous environment of blood and other body fluids!

As for basicity, nonaromatic amines are slightly stronger bases than ammonia, and aromatic amines are weaker bases than ammonia....

Basicity: nonaromatic amines > ammonia > aromatic amines

15.5 Amine Salts

Ammonium salt is composed of a cation and an anion. It occurs when an ammonia (such as methylamine) combines with an acid such as HCl. It is named by combining the ion names. For example...

methylammonium chloride

The salts are generally odorless, white, crystalline solids and they are MUCH MORE SOLUBLE than neutral amines because they are ionic. If a free amine is needed, it is easily regenerated from an amine salt by treatment with a base (opposite of the acid that we started with.)

Quaternary ammonium ions have four organic groups bonded to the N. since it is fully saturated with R groups, there is no H atom to be removed by a base, and no lone pair that can bond with H⁺...so they are not bases AND they are stable in solution. Their sterile storage of medical instruments.

15.6 Amines in Plants: Alkaloids

Plants are a rich source of nitrogen compounds that are basic...these are the alkaloids. Most have a bitter taste and are physiologically active/toxic to humans and animals. Caffeine is an alkaloid, as is nicotine...there are others such as morphine and codeine.

Some common poisonous alkaloids:

- Coniine is extracted from poison hemlock. Think Socrates.
- Atropine is an herb known as deadly nightshade or belladonna. Used as a medication to reduce cramping in the GI tract.
- Solanine is even more potent than atropine...it is found in green potatoes! Also tomatoes. **DON'T EAT IT!**

Not all alkaloids are poisonous...some are pain relievers (analgesics), others are sleep inducers and others provide a euphoric state (think opium, morphine, codein, heroin)