Organic chemistry – crib notes

Amines and Amides

General

Amines and amides are compounds that contain N and are based around the NH_3 molecule. While they are not strictly "organic", they are commonly used in organic reactions as nucleophiles. They are also present in the likes of amino acids (from which DNA is made).

Nitrogen

Nitrogen, like oxygen, has a lone pair of electrons which will give it a negative charge.

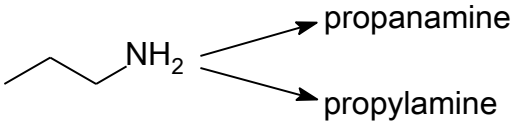
Classification of amines

As with other organic molecules, amines have replaceable hydrogens. This will lead to 1º, 2º and 3º amines. As with alcohols and other carbonyls that show this form of substitution, the 3º is more stable than the 2º which is more stable than the 1º.

Naming amines

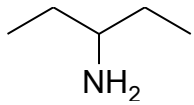
There are two methods of naming amines.

The first is to treat the skeletal as a branch (therefore having an ending of yl) and adding amine to the end. The second is to give the skeletal name followed by amine. Both naming systems are in use.

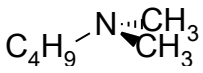


There are a number of exceptions to the normal naming rules

1. If the amine is a branch from a main chain (*right*), it becomes an amino group (3 amino-pentane)



2. If the amine has more than a single substitution and the group is the same (*right*), the *di-* and *tri-* multiplier should be used (butyldimethylamine)



Physical properties

Both 1º and 2º have hydrogens available for hydrogen bonding. This will give them a higher boiling point. 3º amines do not have hydrogens available for hydrogen bonding so will have a lower boiling point. However, 3º amines have a higher molecular mass than a 2º amine which will increase their boiling point to a value close to a 2º amine.

As hydrogen bonding is possible with both 1º and 2º amines, they are soluble in water

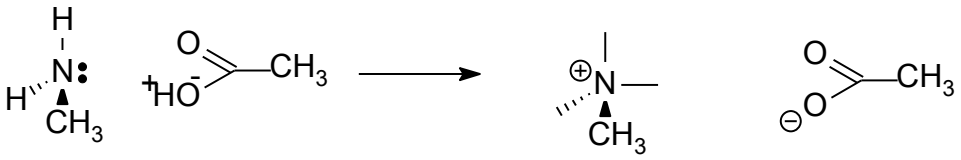
Amines as bases

Amines are strongly influenced by the lone pair of electrons on the nitrogen atom. This lone pair makes nitrogen a very reactive nucleophilic atom. As N is able to accept protons, it acts as a base.

As with all bases, they form a conjugate acid (the stronger the base, the weaker the conjugate acid). With amines when dissolved in water, they form the ammonium conjugate acid. This is a weak acid (pKa = 9.3) which is greatly dwarfed by the strength of the OH^- group also formed.

Amine salts

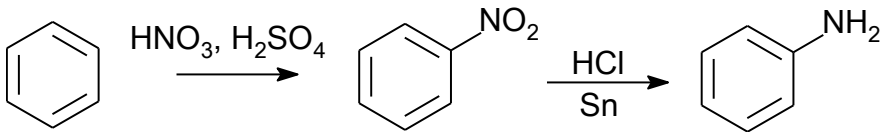
When reacted with an acid (either mineral or organic), amines act as weak bases and form the organic salt (in the same way as an acid and base form the salt). Organic salts can be removed from solution and are commonly used as buffering agents (also known as acidity regulators)



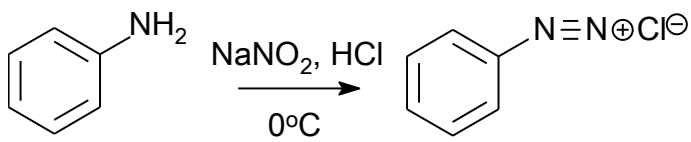
methylamine | methylammonium ion | ethanoate ion

Aromatic amines

Aniline (also known as *phenylamine* or *benzenamine*) is a benzene ring with an NH_2 group attached to it. As NH2 is an nucleophile, the benzene has to be first nitrated and then reacted again to form aniline.



Aniline can then be converted to a “diazonium” salt (this is $N{\equiv}N^+$ group on the phenyl ring) which can then be replaced with other nucleophiles. This saves a lot of time and energy as the benzene no longer needs to be nitrated.



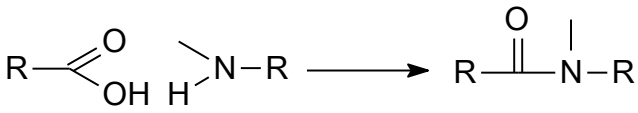
benzenediazonium chloride

The diazonium salt can be replaced by a large number of nucleophiles (including halides directly).

Amides

General

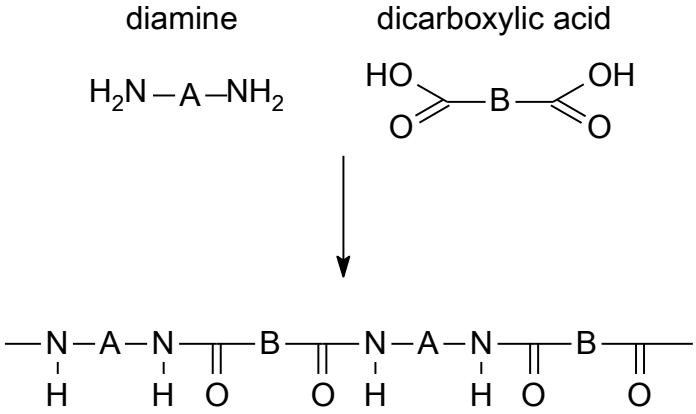
Amides are formed when carboxylic acids and amines react



As there are hydrogens in the amide chain, it is likely to form hydrogen bonds with water and so be soluble (the only notable exception is benzamide which is not soluble).

Polymers

A monomer (*the single unit of a polymer*) containing both the acid and amine is capable of forming polymers.



This route is used frequently for the production of artificial fibres (such as nylon, here A and B are hexane molecules).

Other fibres (such as kevlar) are made in a similar way to nylon.