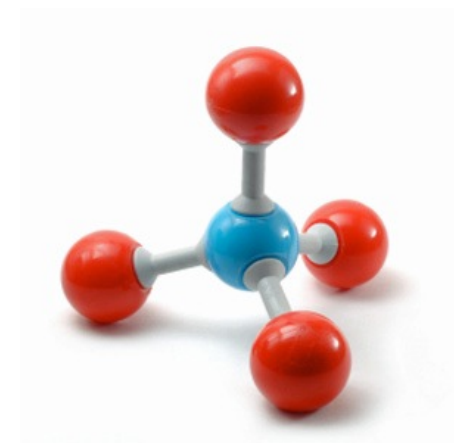


Ch14

Amines & Amides

The fourth element.

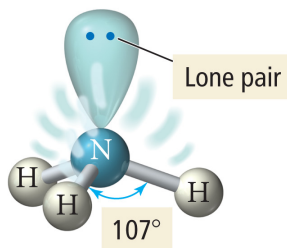
The organic chemistry of nitrogen.



Amines & Amides

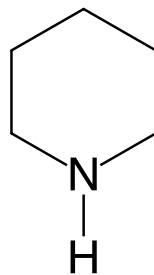
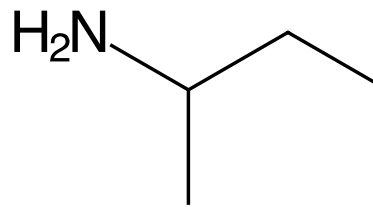
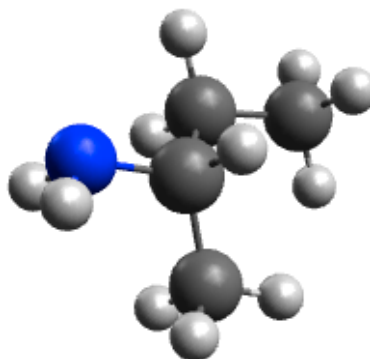
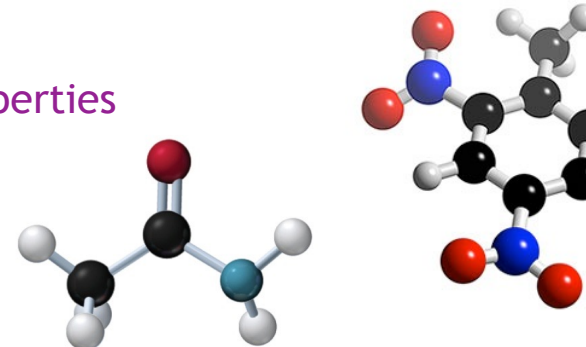
 Nitrogen

- ▶ Ammonia
 - ▶ Structure & Shape
- ▶ Amines
 - ▶ Classifications
 - ▶ Naming & Properties
 - ▶ Amines as bases/salts
 - ▶ Neutralization Rxns
 - ▶ Solubility
 - ▶ Uses
 - ▶ Heterocyclic Amines & Alkaloids

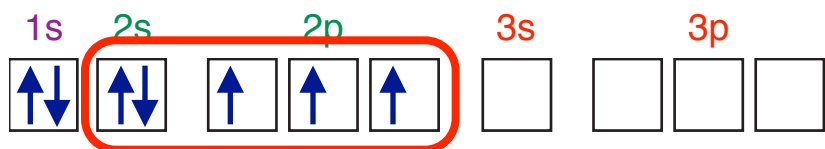


▶ Amides

- ▶ Structure & Properties
- ▶ Naming
- ▶ Reactions
 - ▶ Amidation
 - ▶ Hydrolysis



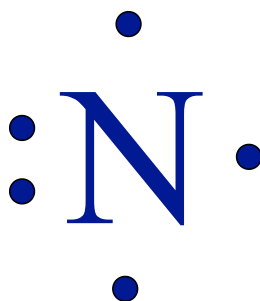
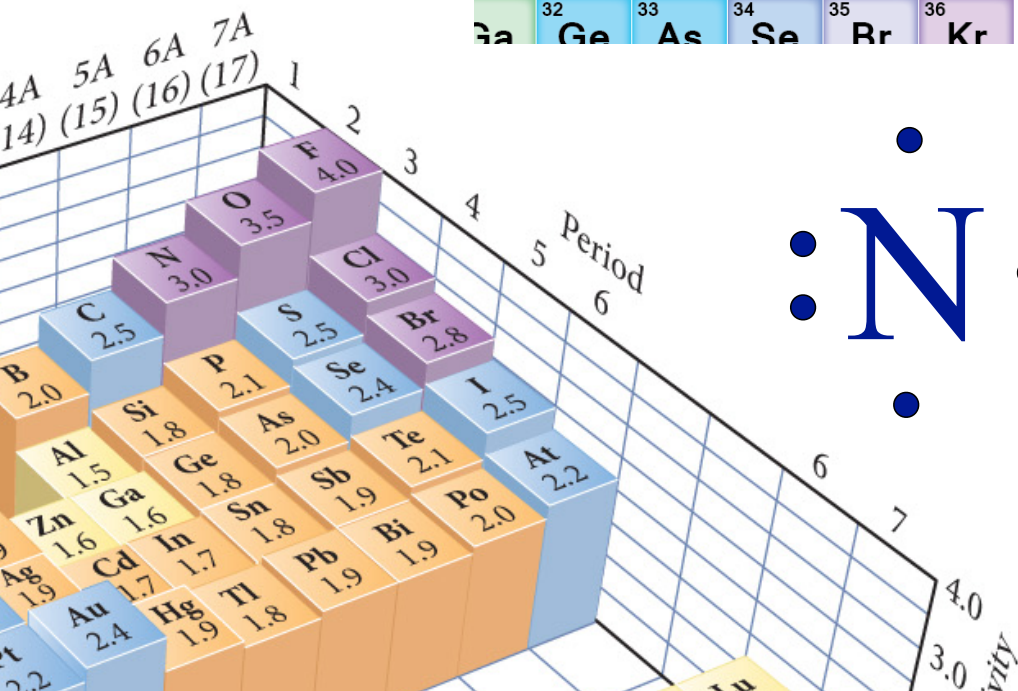
Nitrogen



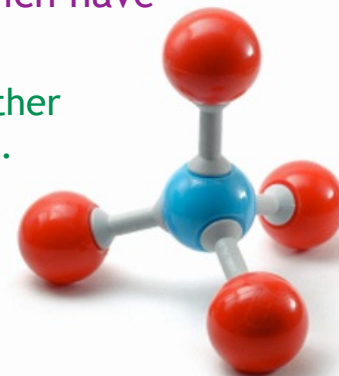
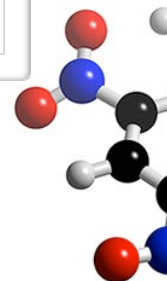
7 electrons

5 valence electrons

					2 VIII A 8A He Helium 4.003
6 IIIA 3A B Boron 10.811	7 IVA 4A C Carbon 12.011	8 VA 5A N Nitrogen 14.007	9 VIA 6A O Oxygen 15.999	10 VIIA 7A F Fluorine 18.998	18 Ne Neon 20.180
14 IIIA 3A Al Aluminum 26.982	15 IVA 4A Si Silicon 28.086	16 VA 5A P Phosphorus 30.974	17 VIA 6A S Sulfur 32.066	18 VIIA 7A Cl Chlorine 35.453	18 Ar Argon 39.948
32 IIIA 3A Ga	33 IVA 4A Ge	34 VA 5A As	35 VIA 6A Se	36 VIIA 7A Br	36 Kr



- ▶ Organic chemistry is the chemistry of **CARBON & HYDROGEN**.
- ▶ Understanding **OXYGEN** opens up the functionality of alcohols, ketones, aldehydes, carboxylic acids, esters, ethers and more.
- ▶ After these elements, **NITROGEN** is the next most important element in organic chemistry.
 - ▶ The fourth most electronegative (EN) element.
 - ▶ Chlorine is very slightly more EN.
 - ▶ Has 5 valence electrons.
 - ▶ Makes -3 monatomic anions; -1 oxy-ions
 - ▶ Usually forms 3 (sometimes 4) bonds.
 - ▶ One of only three elements (O, N, F) that produce substances which have hydrogen bonding.
 - ▶ Cl is too big and no other element is EN enough.
 - ▶ A non-metal.



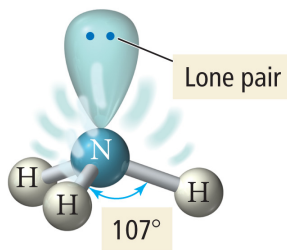
Amines & Amides

▶ Nitrogen



Ammonia

▶ Structure & Shape



▶ Amines

▶ Classifications

▶ Naming & Properties

▶ Amines as bases/salts

▶ Neutralization Rxns

▶ Solubility

▶ Uses

▶ Heterocyclic Amines & Alkaloids

▶ Amides

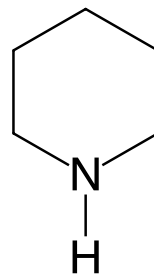
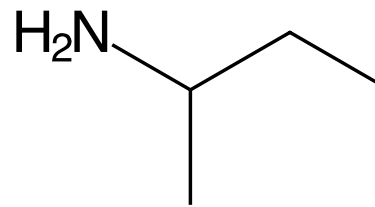
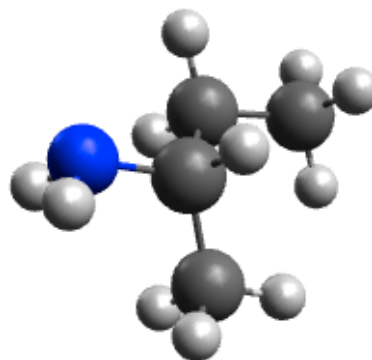
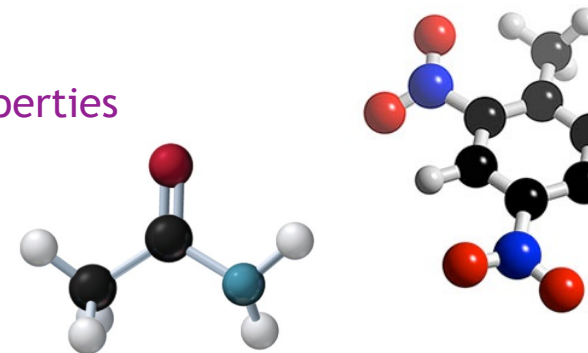
▶ Structure & Properties

▶ Naming

▶ Reactions

▶ Amidation

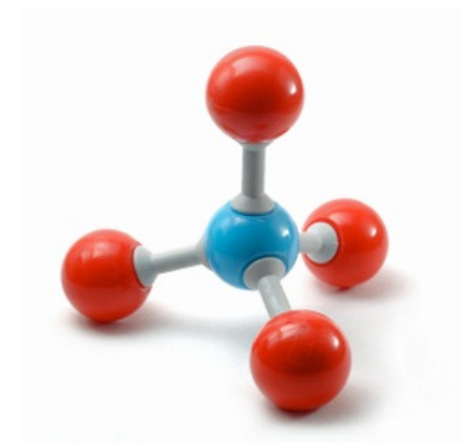
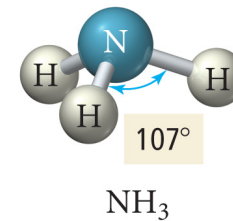
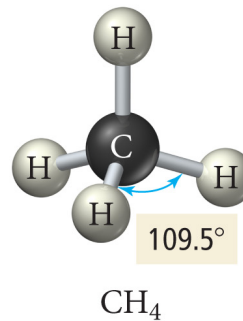
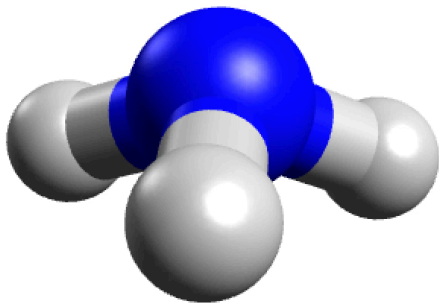
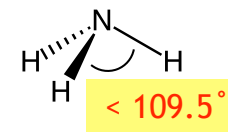
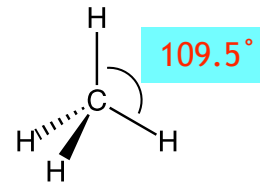
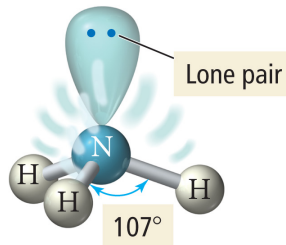
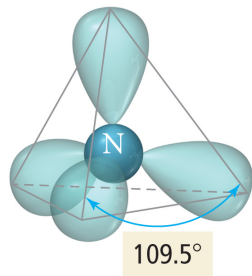
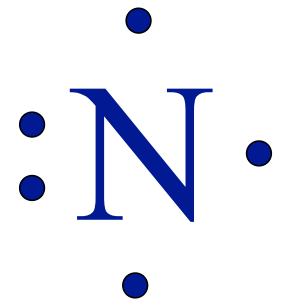
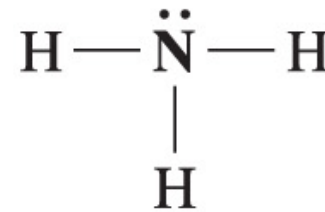
▶ Hydrolysis



Ammonia

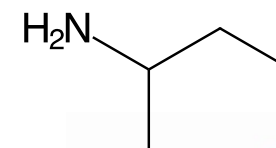
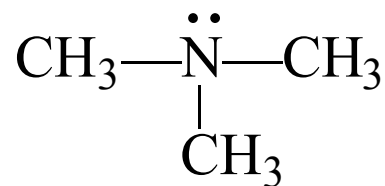
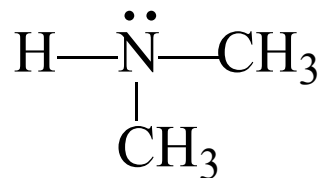
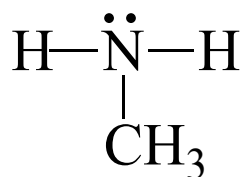
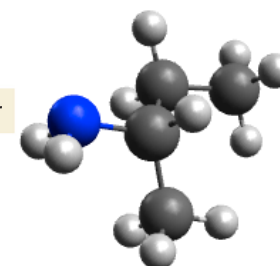
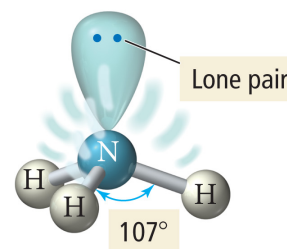
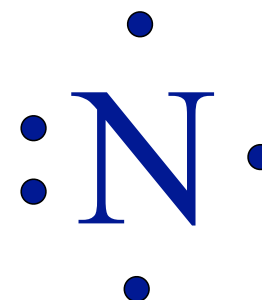
- ▶ Ammonia (NH₃) has tetrahedral electronic shape (electrons around the atom).
- ▶ Ammonia has a trigonal pyramidal geometric shape (bonds around the atom).
 - ▶ Not trigonal planar!

Ammonia



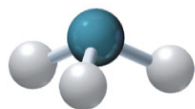
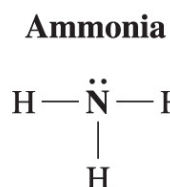
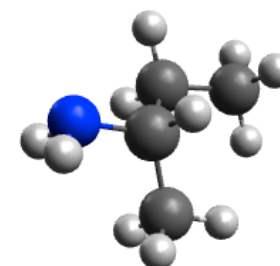
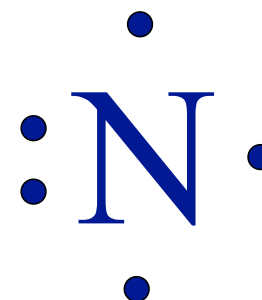
Amines

- ▶ Amines have one or more carbon atoms bonded to the N atom.
- ▶ Amines are classified as primary, secondary, or tertiary:
 - ▶ A primary (1°) amine has one carbon bonded to the nitrogen atom.
 - ▶ A secondary (2°) amine has two carbon bonded to the nitrogen.
 - ▶ A tertiary (3°) amine has three carbon bonded to the nitrogen.

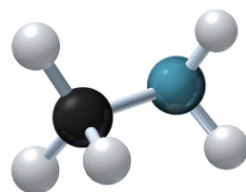
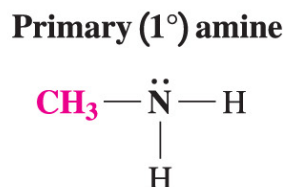


Amines

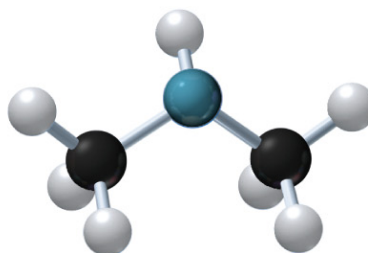
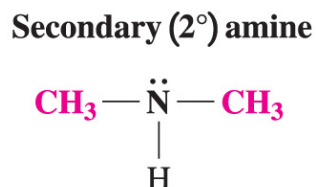
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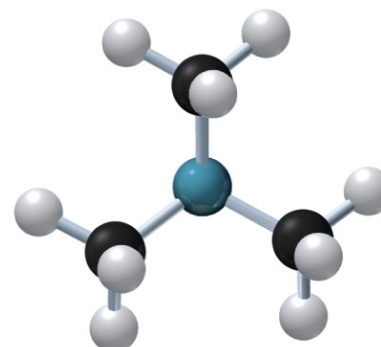
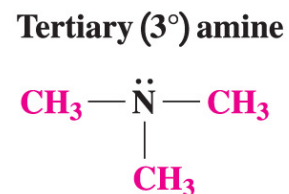
Ammonia



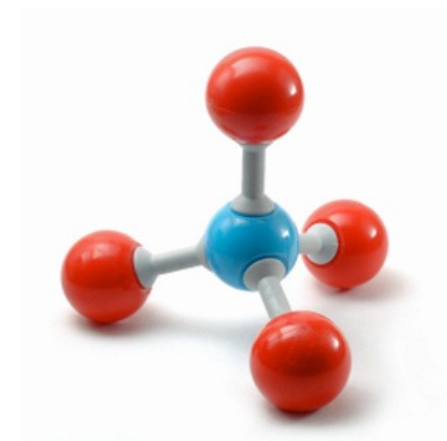
Methylamine



Dimethylamine

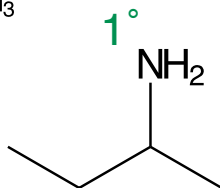
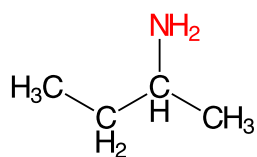
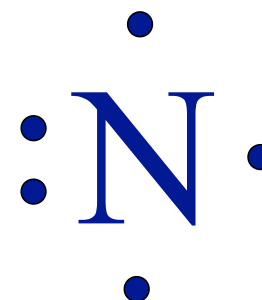


Trimethylamine

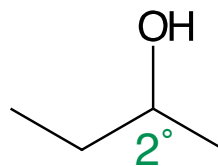
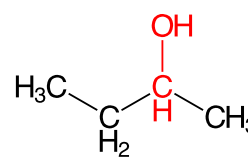


Amines

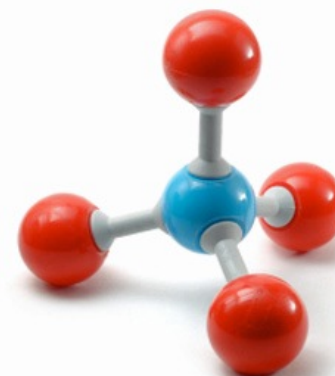
- ▶ Amines have one or more carbon atoms bonded to the N atom.
- ▶ Amines are classified as primary, secondary, or tertiary:
 - ▶ A primary (1°) amine has one carbon bonded to the nitrogen atom.
 - ▶ A secondary (2°) amine has two carbon bonded to the nitrogen.
 - ▶ A tertiary (3°) amine has three carbon bonded to the nitrogen.
- ▶ This is **not the same** as how we classify alcohols!
 - ▶ We classify alcohols by the number of carbon atoms bonded to the **carbon atom** on which the alcohol is located.



Primary (1°)
Amine

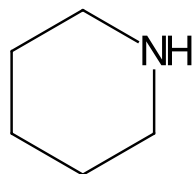
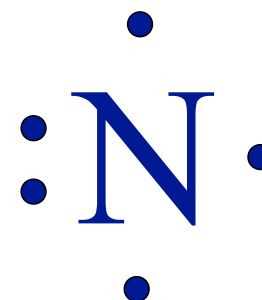


Secondary (2°)
Alcohol

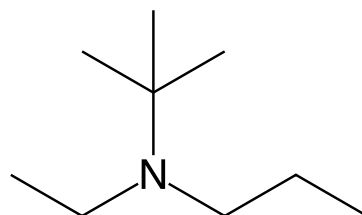


Amines

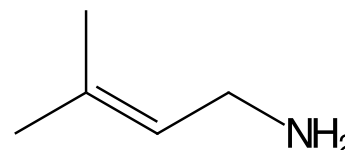
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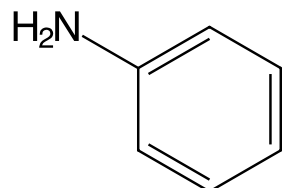
Secondary (2°)



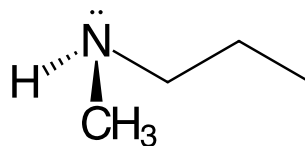
Tertiary (3°)



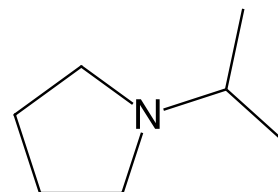
Primary (1°)



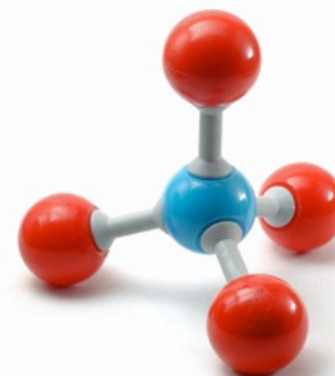
Primary (1°)



Secondary (2°)

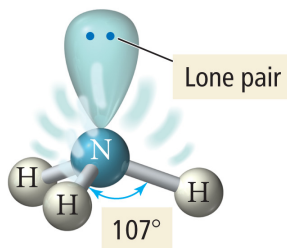


Tertiary (3°)

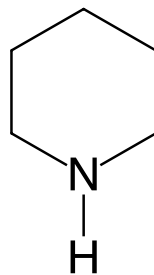
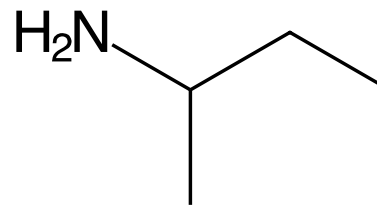
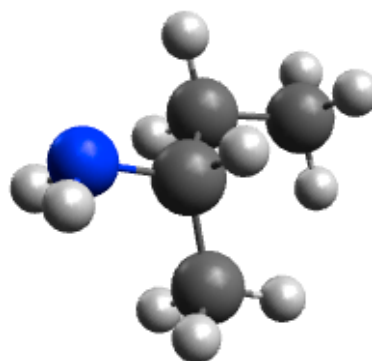
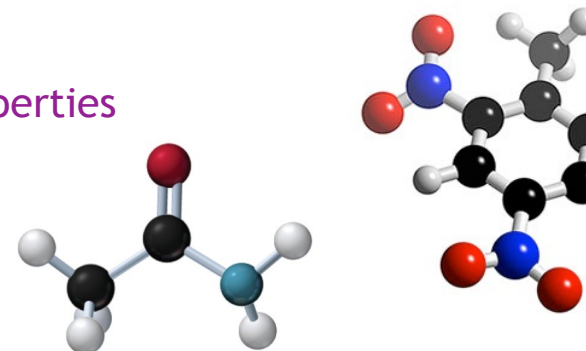


Amines & Amides

- ▶ Nitrogen
- ▶ Ammonia
 - ▶ Structure & Shape
- ▶ Amines
 - ▶ Classifications
 - ▶ Naming & Properties
 - ▶ Amines as bases/salts
 - ▶ Neutralization Rxns
 - ▶ Solubility
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- ▶ Amides
 - ▶ Structure & Properties
 - ▶ Naming
 - ▶ Reactions
 - ▶ Amidation
 - ▶ Hydrolysis



Amines

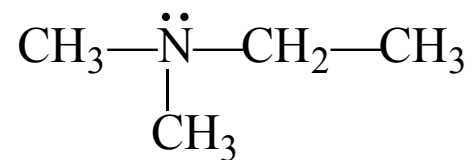
- ▶ Simple amines are named as alkylamines
 - ▶ list the names of the alkyl groups bonded to the N atom
 - ▶ in alphabetical order in front of “amine” (like ethers)
 - ▶ use prefixes to identify duplicate alkyl substituents



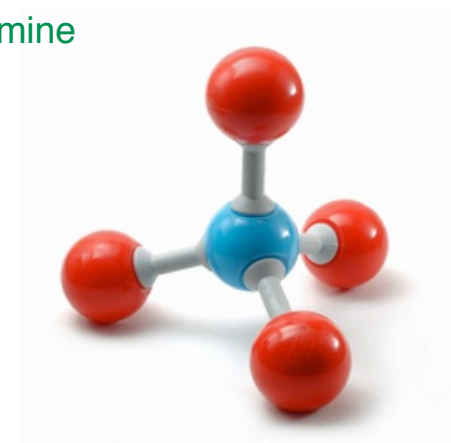
Ethylamine



Dimethylamine

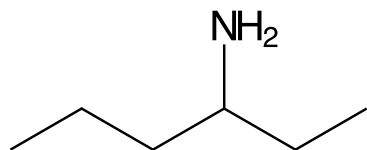


Ethyldimethylamine

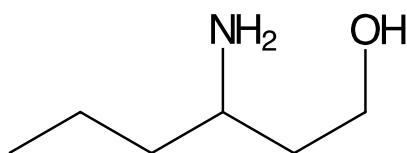


Amines

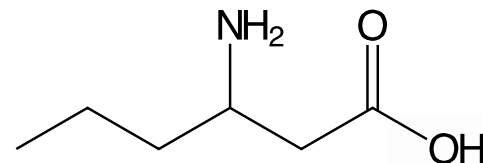
- ▶ Simple amines are named as alkylamines
 - ▶ list the names of the alkyl groups bonded to the N atom
 - ▶ in alphabetical order in front of “amine” (like ethers)
 - ▶ use prefixes to identify duplicate alkyl substituents
- ▶ If the amine is in another organic family (for example if there is a hydroxy or carboxyl group) it becomes the “amino” group.



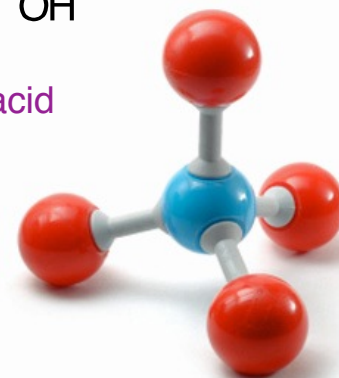
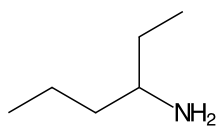
1-Ethylbutylamine



3-Aminohexanol



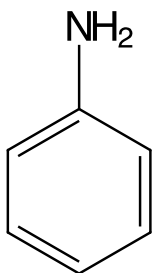
3-Aminohexanoic acid



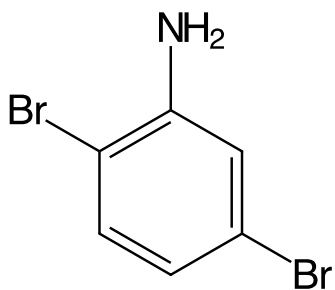
Amines

- ▶ Aromatic amines are named as anilines.
 - ▶ the amine of benzene is aniline.
 - ▶ List the names of the alkyl groups bonded to the ring.
 - ▶ in alphabetical order in front of “aniline” (like toluene)
 - ▶ use prefixes to identify duplicate alkyl substituents
 - ▶ show their address relative to the N in aniline
 - ▶ Substituents attached to the N nitrogen are prefixed with “N” instead of a number.

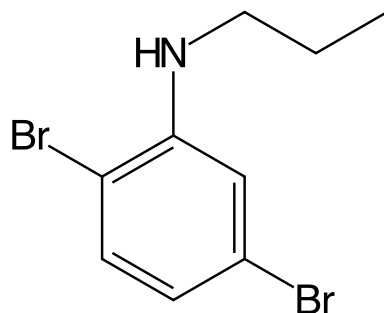
Aniline



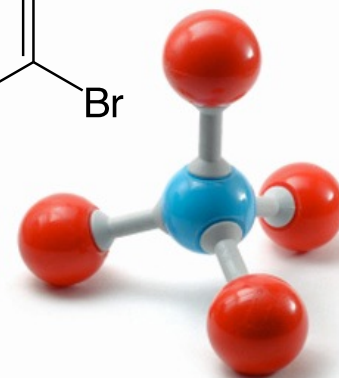
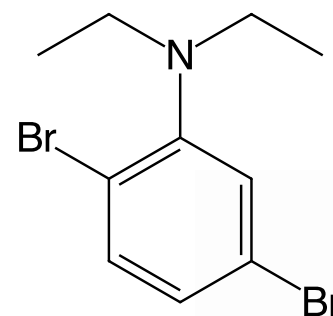
2,5-Dibromoaniline



2,5-dibromo-N-propyl-aniline

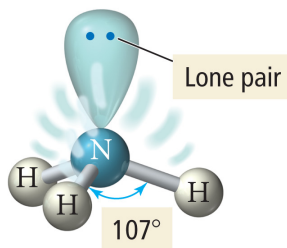


2,5-dibromo-N,N-Diethyl-aniline

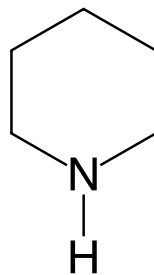
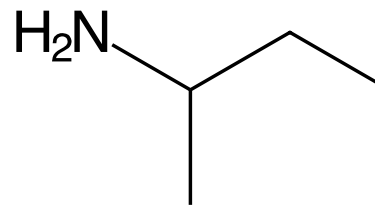
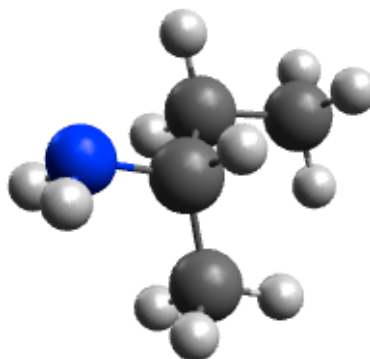
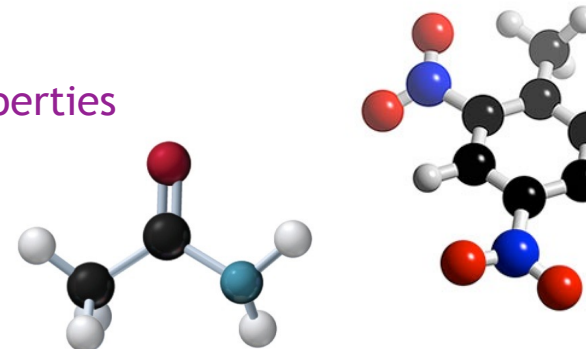


Amines & Amides

- ▶ Nitrogen
- ▶ Ammonia
 - ▶ Structure & Shape
- ▶ Amines
 - ▶ Classifications
 - ▶ Naming & Properties
 - ▶ Amines as bases/salts
 - ▶ Neutralization Rxns
 - ▶ Solubility
 - ▶ Uses
 - ▶ Heterocyclic Amines & Alkaloids



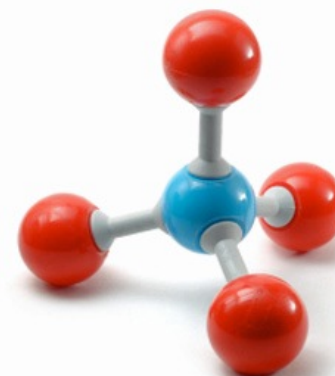
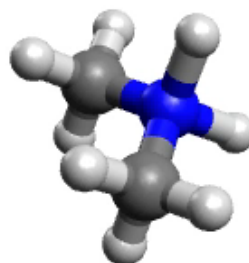
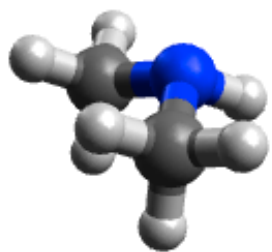
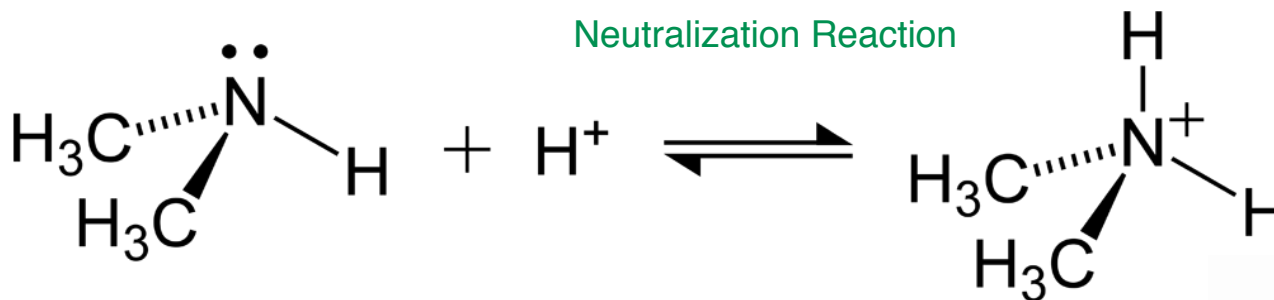
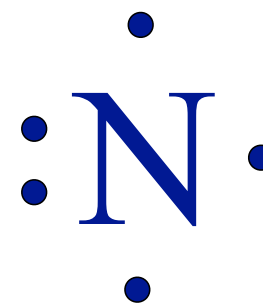
- ▶ Amides
 - ▶ Structure & Properties
 - ▶ Naming
 - ▶ Reactions
 - ▶ Amidation
 - ▶ Hydrolysis



Ammonium Ions

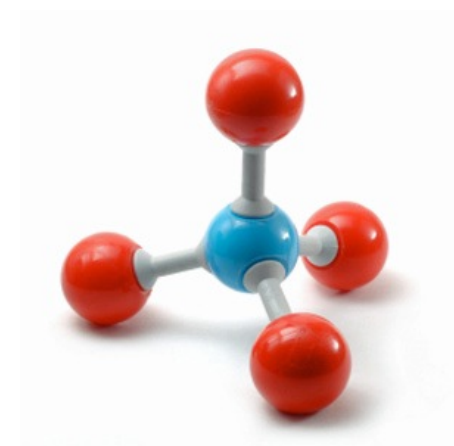
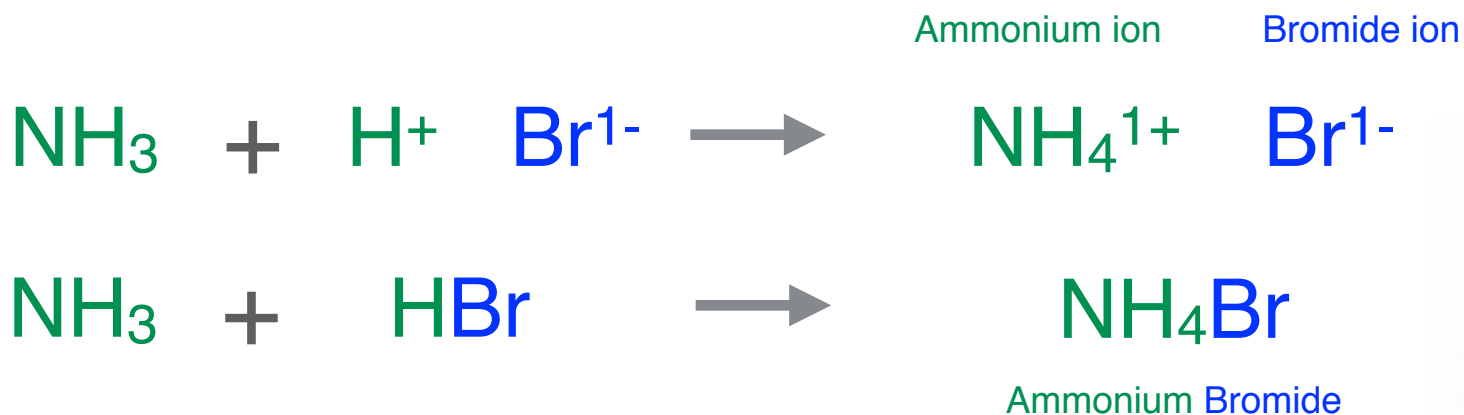
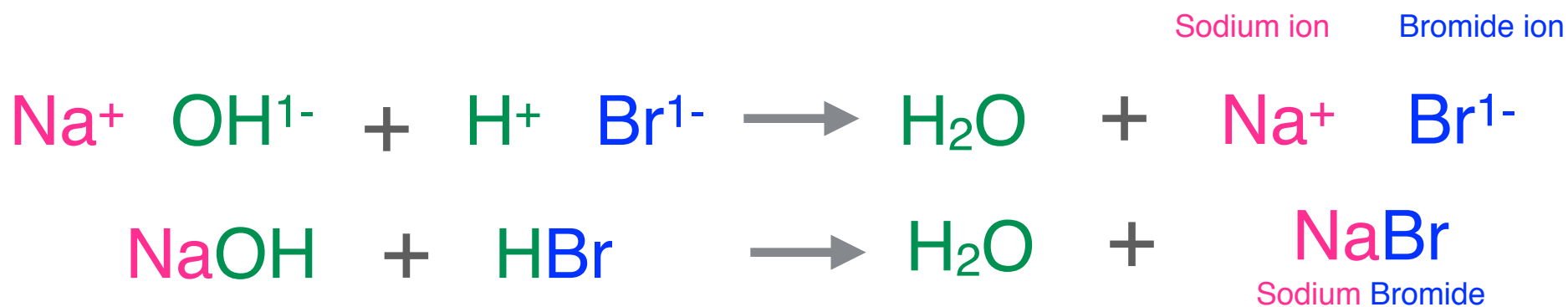
Ammonium ion (NH_4^+) may have been one of the polyatomic ions you learned last quarter.

- ▶ The Brønsted-Lowry description of acids and bases:
 - ▶ **Acids** are substances that release protons.
 - ▶ **Bases** are substances that accept protons.
- ▶ Amines can act as bases to produce ammonium ions.
- ▶ Ammonium ions are acids.
 - ▶ Ammonium ions have four bonds and a tetrahedral structure.



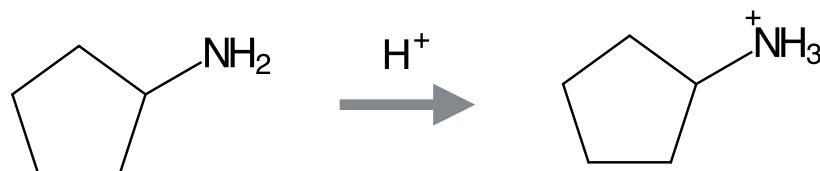
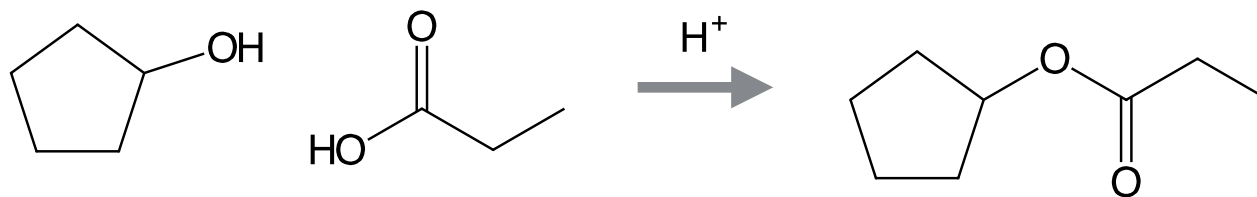
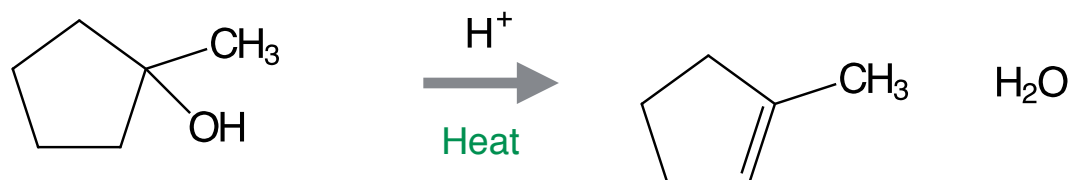
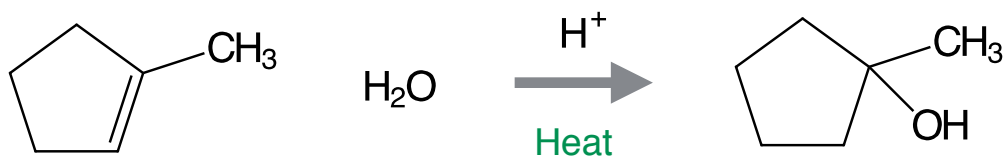
Ammonium Ions

- ▶ Reacting an acid with a base is a **neutralization** reaction.
- ▶ Amines form Ammonium ion, instead of water when neutralized.



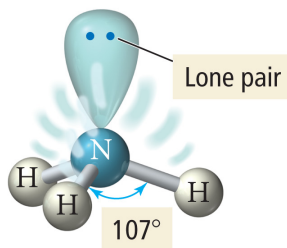
Ammonium Ions

- ▶ Neutralization of amines is one more acid reaction to add to your toolbox.
 - ▶ You have four now.
- ▶ Predict the product of each reaction.

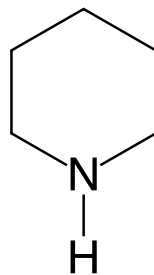
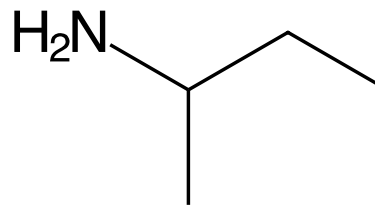
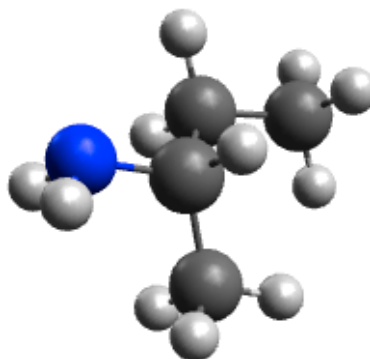
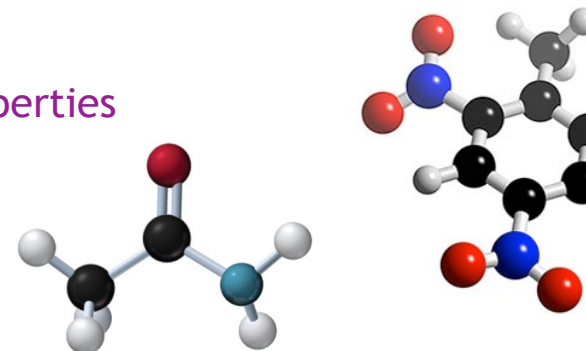


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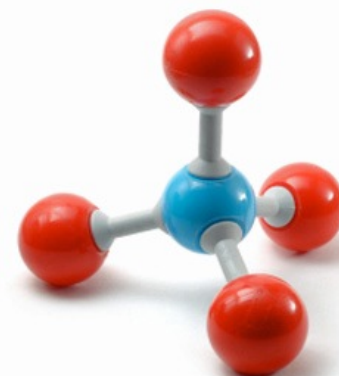


- ▶ Amides
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 - ▶ Amidation
 - ▶ Hydrolysis



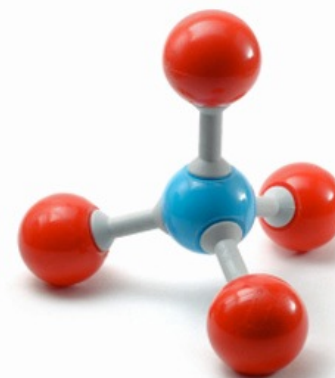
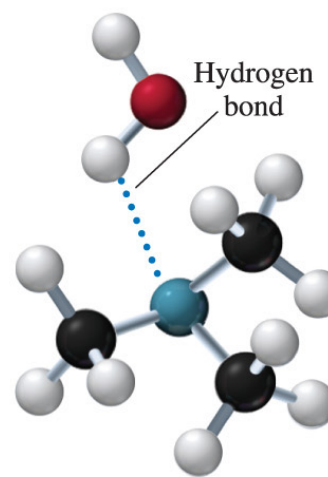
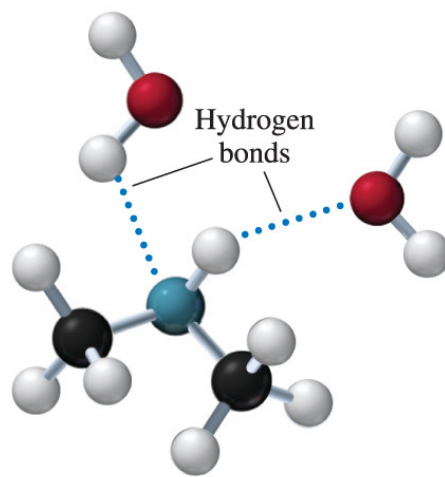
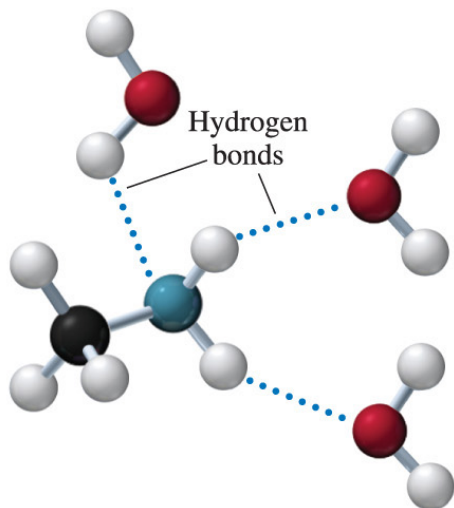
Properties of Amines

- ▶ Distinctive odors that are fishy to putrid characterize the lower-molecular-weight amines. They are gases at room temperature or are easily vaporized liquids.
- ▶ With increasing size, they become less volatile; the odor decreases and eventually becomes unnoticeable, although some diamines have offensive odors.
 - ▶ For example, $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$, called putrescine, and $\text{H}_2\text{N}(\text{CH}_2)_5\text{NH}_2$, called cadaverine, are foul-smelling compounds found in decaying flesh.
- ▶ Most aliphatic amines are not highly toxic, and many are harmless, natural components of foods and pharmaceuticals.
 - ▶ In high concentrations, however, the smaller amines are highly irritating to the skin and especially to the mucous membranes of the eyes, nose, throat, and lungs, to which they can cause acute damage upon prolonged exposure.
 - ▶ Larger amines (12 or more carbon atoms) are usually less irritating.
 - ▶ Aromatic amines are also irritants and can be absorbed through the skin. They may be dangerous poisons.
 - ▶ Aniline, for example, destroys the hemoglobin of blood, and prolonged exposure has been linked with cancer.
 - ▶ Amines can be corrosive to some metals and plastics.



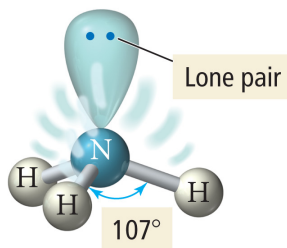
Properties of Amines

- ▶ Because amines contain a polar N –H bond, they form hydrogen bonds with water.
 - ▶ Primary (1°) amines, -NH_2 , can form more hydrogen bonds than the secondary (2°) amines.
 - ▶ Tertiary (3°) amines have no hydrogen on the nitrogen atom and can form only hydrogen bonds with water from the N atom.
- ▶ Amines with less than six carbons are soluble in water.
 - ▶ Like alcohols, the smaller amines, including tertiary ones, are soluble because they form hydrogen bonds with water.
- ▶ Alkyl amines are less dense than water, having densities in the range 0.63 to 0.74 gram per cubic cm.
 - ▶ Aromatic amines are typically slightly heavier than water (e.g., the density of aniline is 1.02 grams per cubic cm).

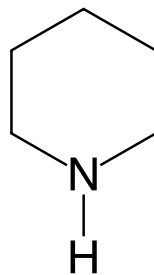
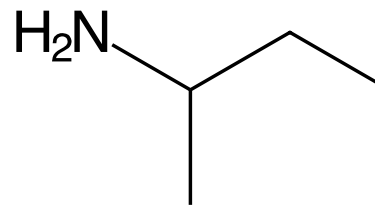
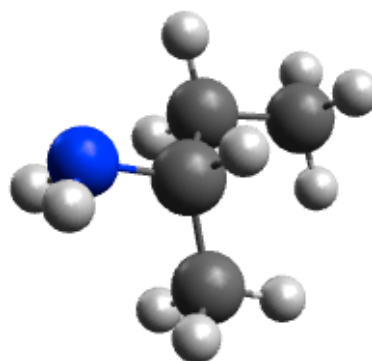
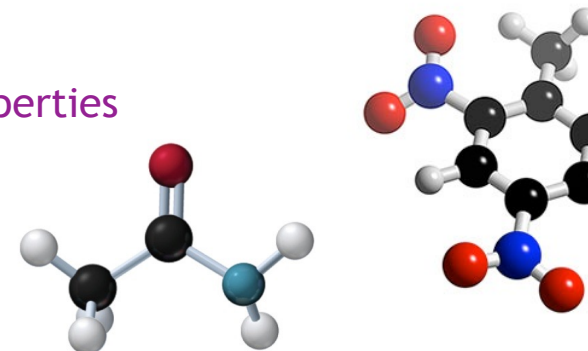


Amines & Amides

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- Uses
 - ▶ Heterocyclic Amines & Alkaloids

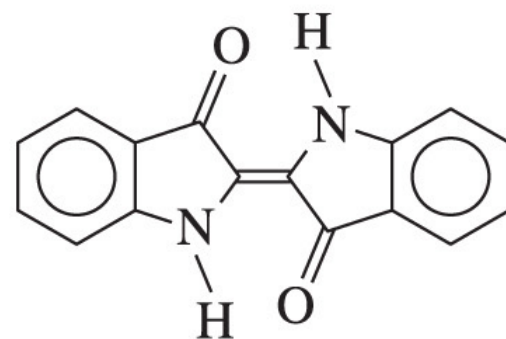


- ▶ Amides
 - ▶ Structure & Properties
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 - ▶ Reactions
 - ▶ Amidation
 - ▶ Hydrolysis



Uses of Amines

- ▶ Amines exist in many natural products.
- ▶ Amines are used in making rubber, dyes, pharmaceuticals, and synthetic fibres.
- ▶ The color indigo was named after the indigo dye derived from the plant *Indigofera tinctoria* and related species, a naturally occurring amine.
 - ▶ Indigo has had widespread use through out the world as tattoo ink and dye for clothing.



Indigo

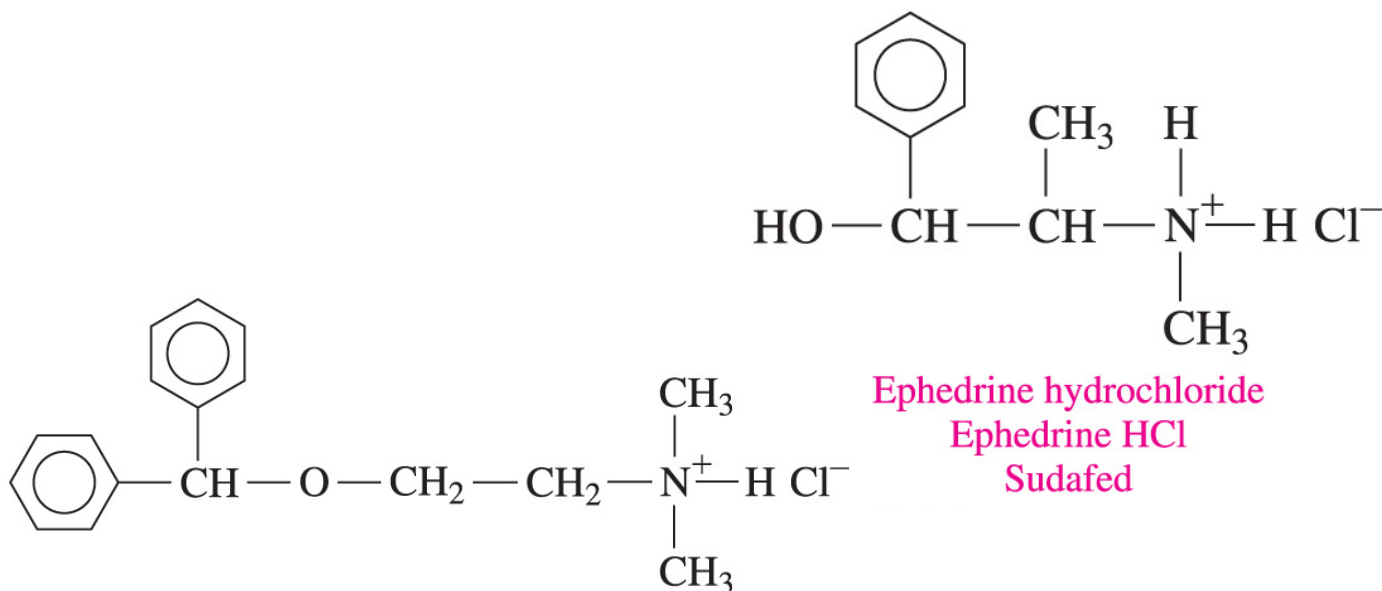


Indigofera tinctoria



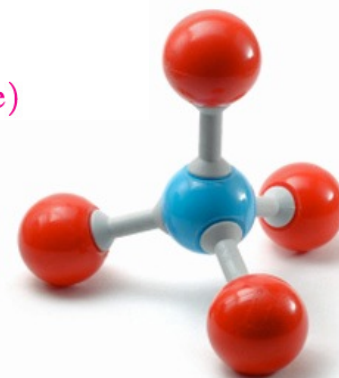
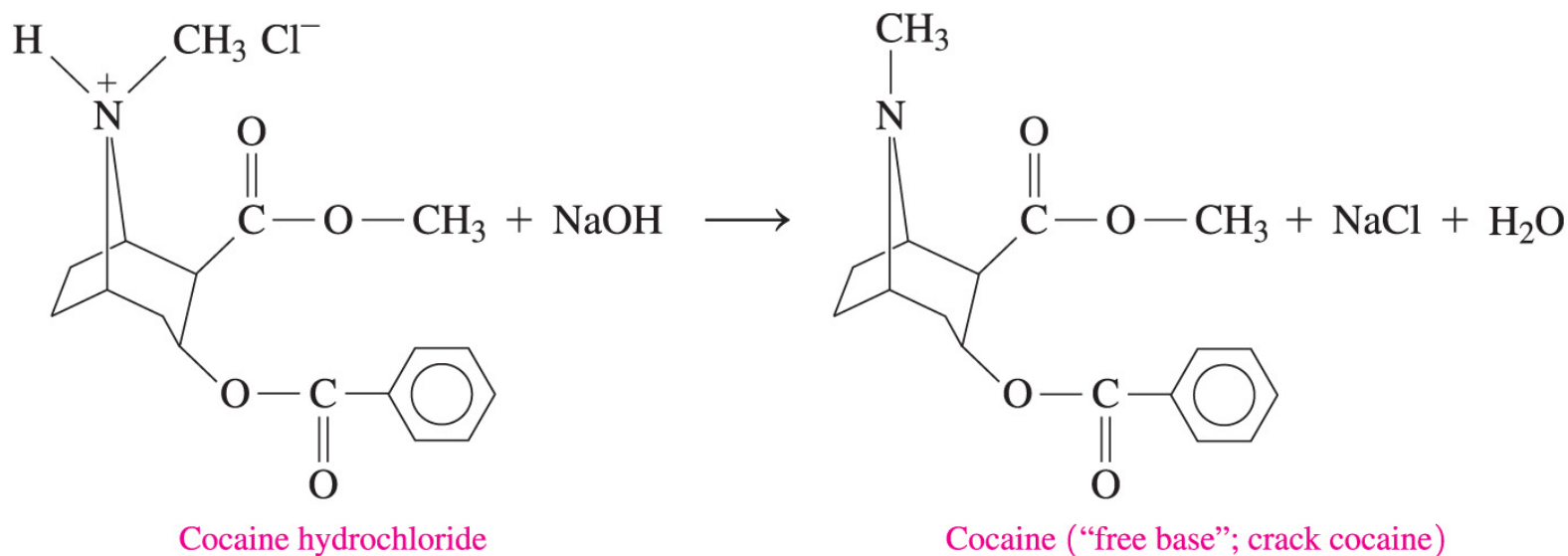
Uses of Amines

- ▶ Amines are usually converted to their ammonium salt before being used as drugs.
- ▶ The ammonium salts are solids at room temperature, odorless and soluble in water and body fluids.
- ▶ Ammonium salts are used as the active ingredients in medications:
 - ▶ Ephedrine is used as a bronchodilator in the decongestant Sudafed.
 - ▶ Diphenylhydramine, found in Benadryl, is used for relief of itching and pain from skin irritations and rashes.



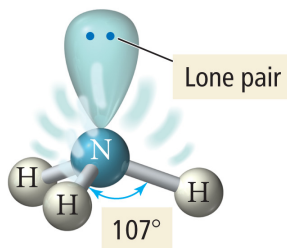
Uses of Amines

- ▶ The narcotic cocaine, extracted from coca leaves using an acidic HCl solution, is smuggled and used illegally in the form of cocaine hydrochloride, an ammonium salt.
- ▶ Cocaine hydrochloride, an ammonium salt, can be converted back to its free amine or free base form, “crack cocaine” by treating it with a strong base.

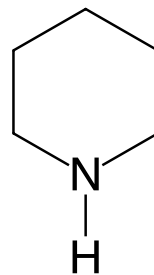
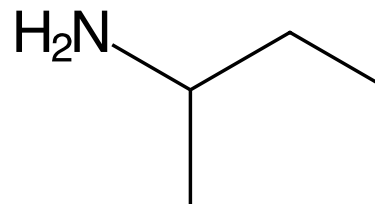
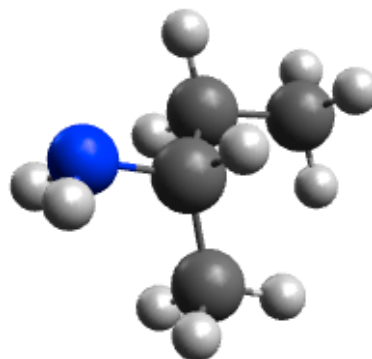
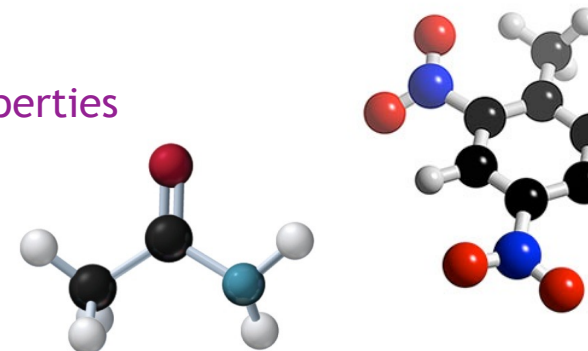


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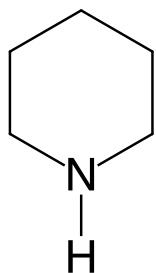
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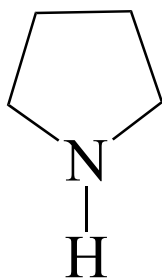
Heterocyclic Amines

- ▶ A **heterocycle** is a ring compound composed of carbon and other elements.
- ▶ Heterocyclic amines with five or six atoms in the ring with one or more nitrogen atoms are common and produce many biologically active substances.
- ▶ Piperidine, a heterocyclic amine, is responsible for the aroma in black pepper.
- ▶ Fructofuranose, another heterocyclic compound, is a sugar.

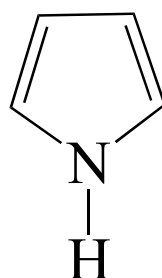
Piperidine



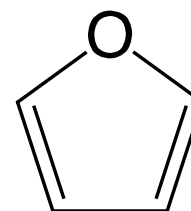
Pyrrolidine



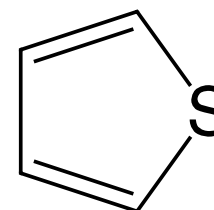
Pyrrole



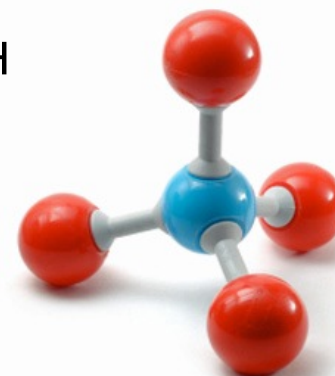
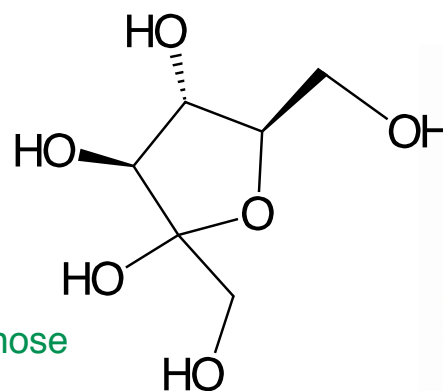
Furan



Thiophene

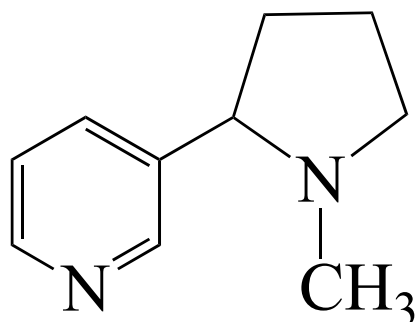


Fructofuranose

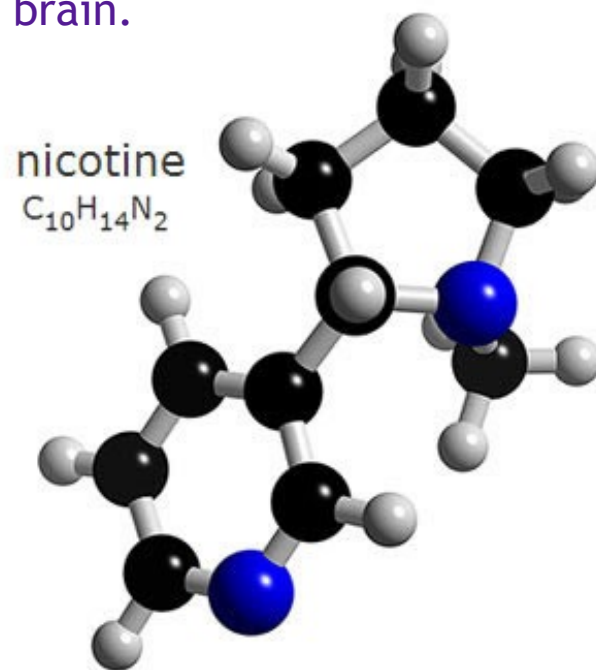


Alkaloids

- ▶ **Alkaloids** are a group of naturally occurring chemical compounds that contain mostly basic nitrogen atoms.
- ▶ Alkaloids are
 - ▶ physiologically active compounds produced by plants that contain heterocyclic amines
 - ▶ used in anesthetics, in antidepressants, and as stimulants, and many are habit forming
- ▶ Nicotine is a stimulant that increases
 - ▶ the level of adrenaline in the blood
 - ▶ heart rate and blood pressure
- ▶ Nicotine is addictive because it activates pleasure centers in the brain.



Nicotine

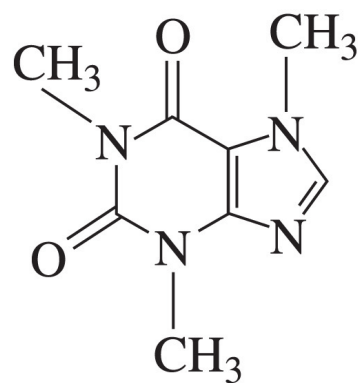
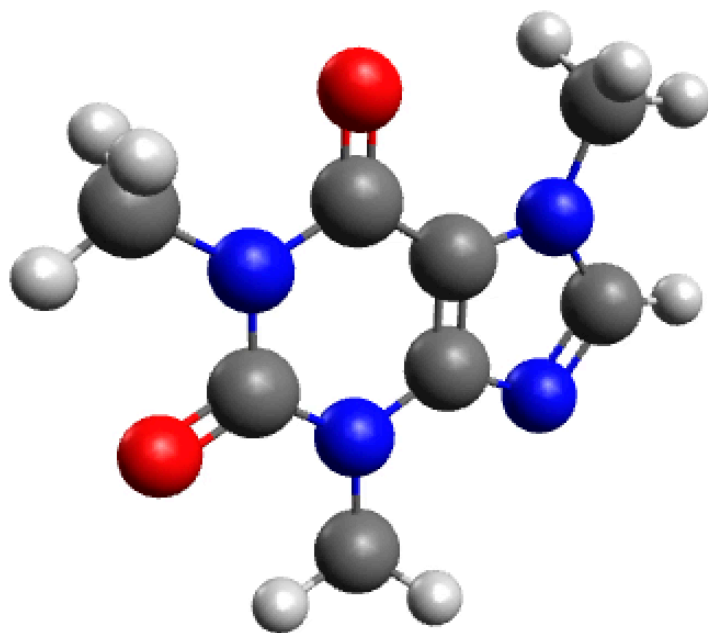


nicotine
 $C_{10}H_{14}N_2$

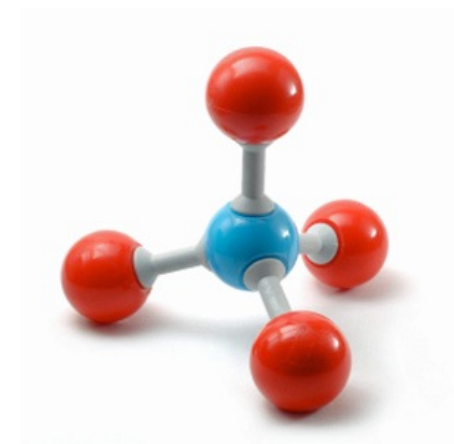
Alkaloids

▶ Caffeine

- ▶ is an alkaloid found in coffee beans, tea, chocolate, and soft drinks
- ▶ is a stimulant of the central nervous system
- ▶ increases alertness but may cause insomnia

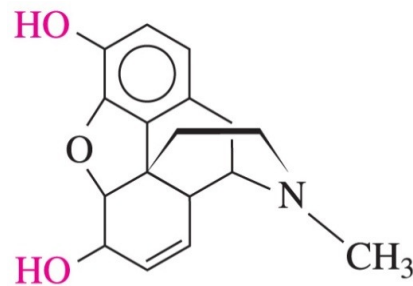


Caffeine

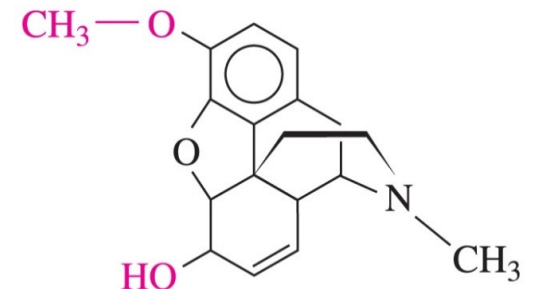


Alkaloids

- ▶ Morphine and codeine are alkaloids
 - ▶ obtained from the poppy plant
 - ▶ used as painkillers
 - ▶ very addictive

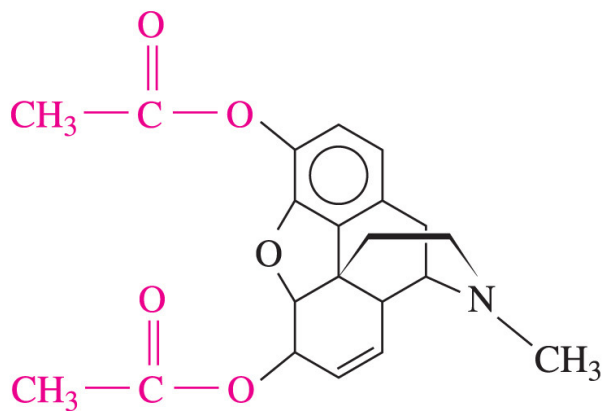


Morphine

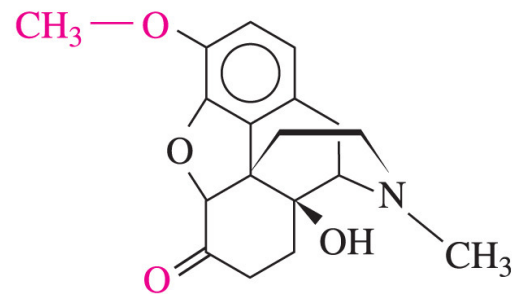


Codeine

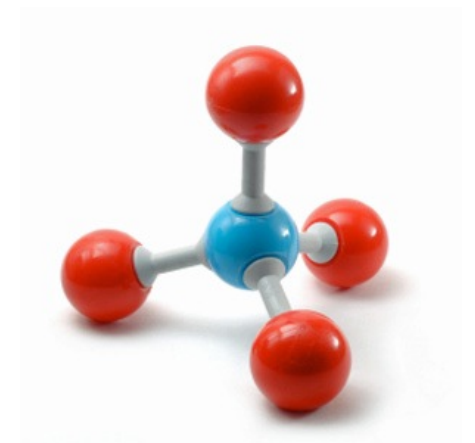
- ▶ Heroin and oxycontin (oxycodone) are synthetic alkaloids with similar reactivity.



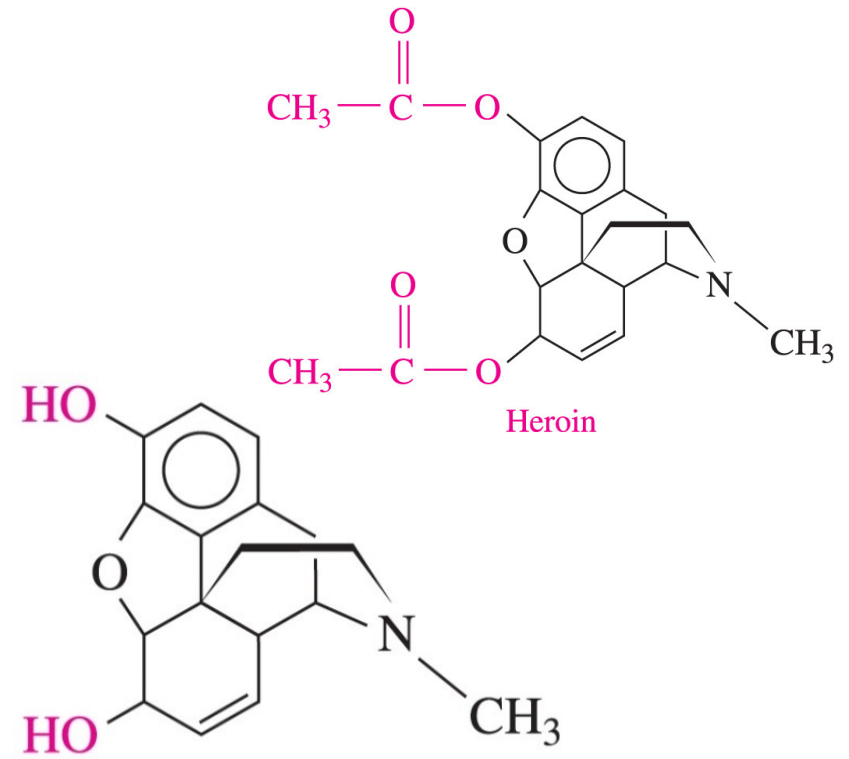
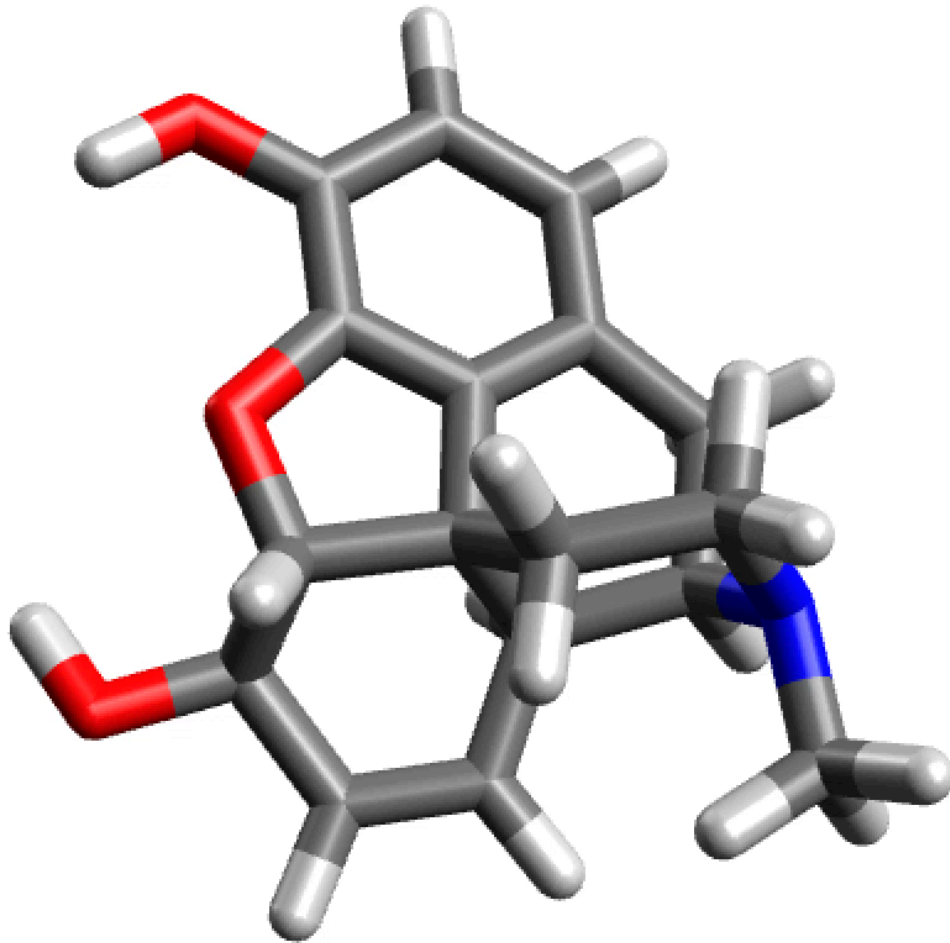
Heroin



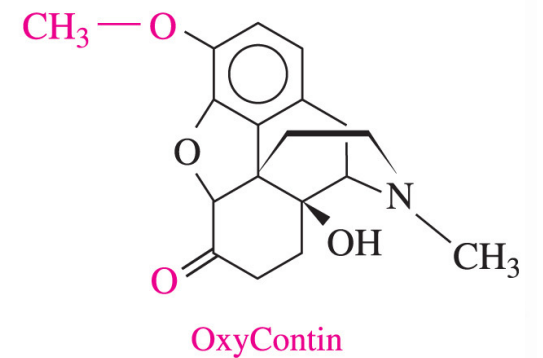
OxyContin



Alkaloids

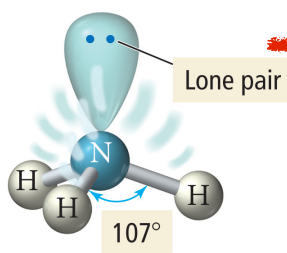


Morphine



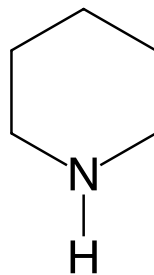
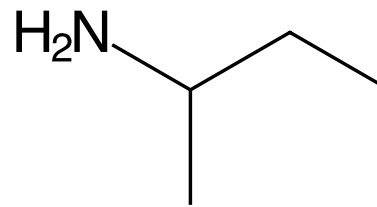
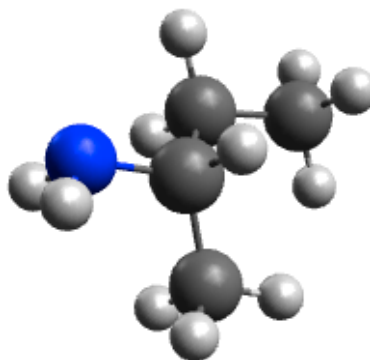
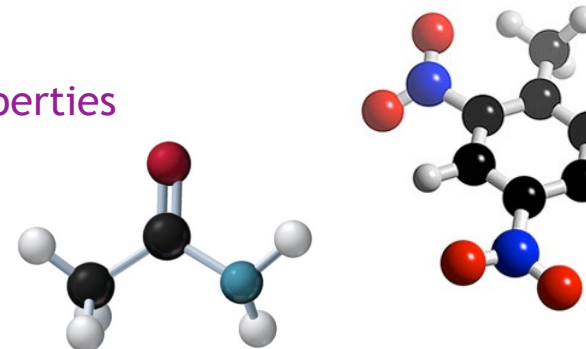
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Amides

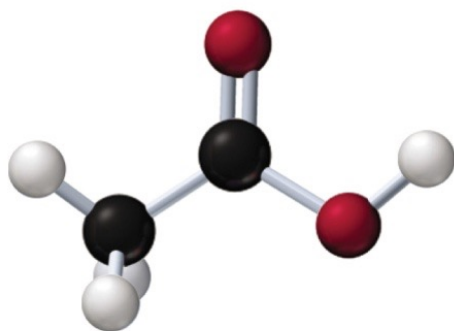
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Amides

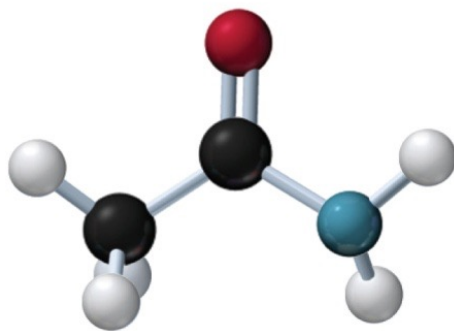
- ▶ **Amides** are derivatives of carboxylic acids in which a nitrogen group ($-\text{NH}_2$) replaces the hydroxyl ($-\text{OH}$) group of carboxylic acids.
- ▶ They contain the carboxamide functional group ($-\text{CON}-$).
 - ▶ This group is also called an amino carboxyl or sometimes just amide.

Carboxylic Acid

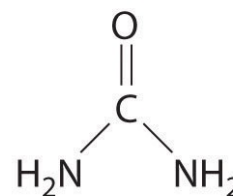


Ethanoic acid
(acetic acid)

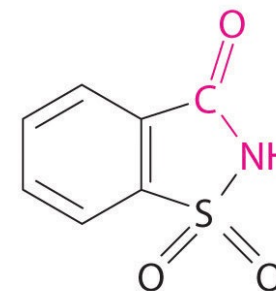
Amide



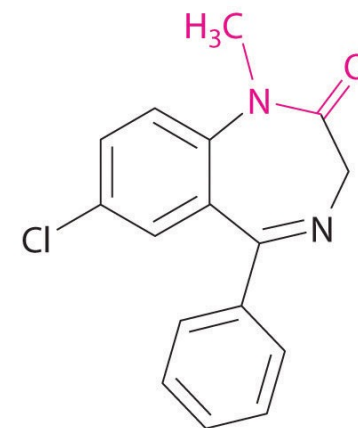
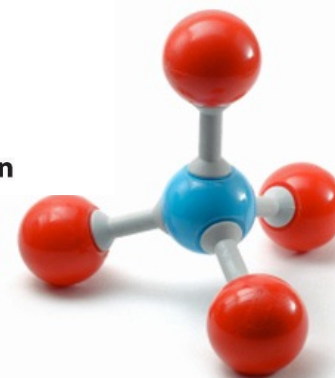
Ethanamide
(acetamide)



Urea



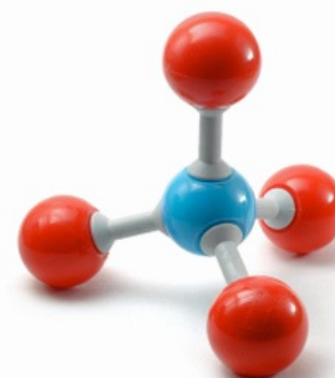
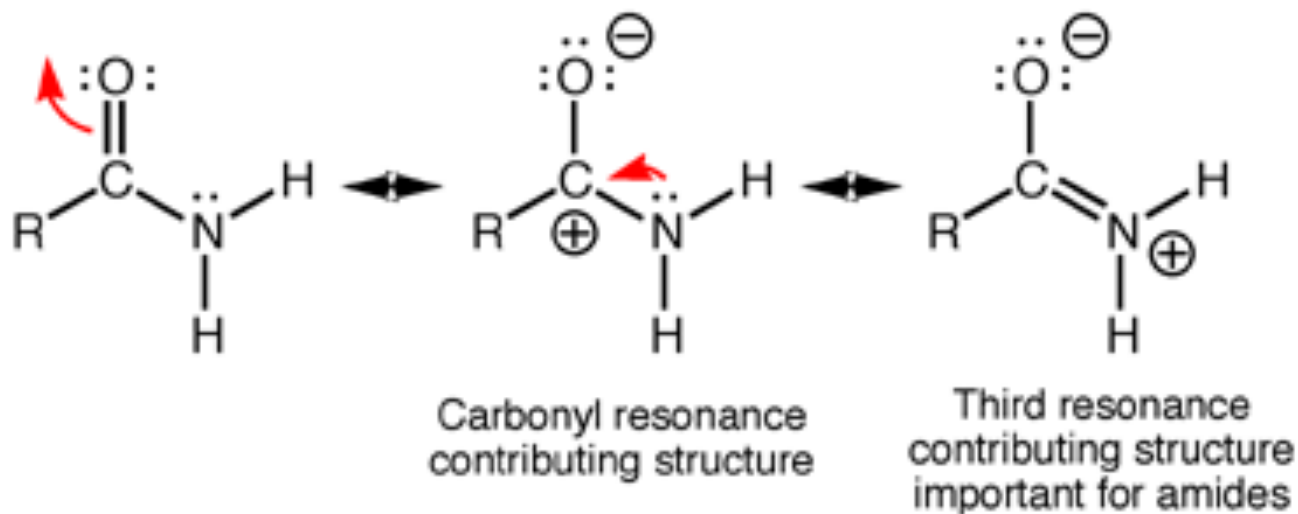
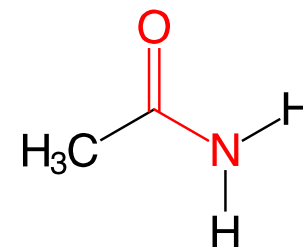
Saccharin



Valium

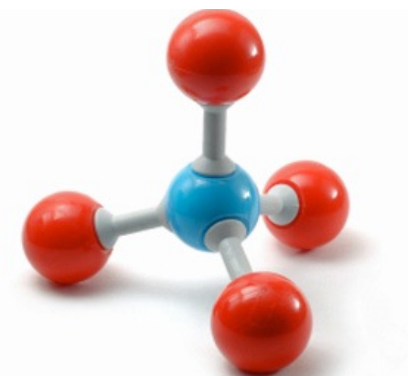
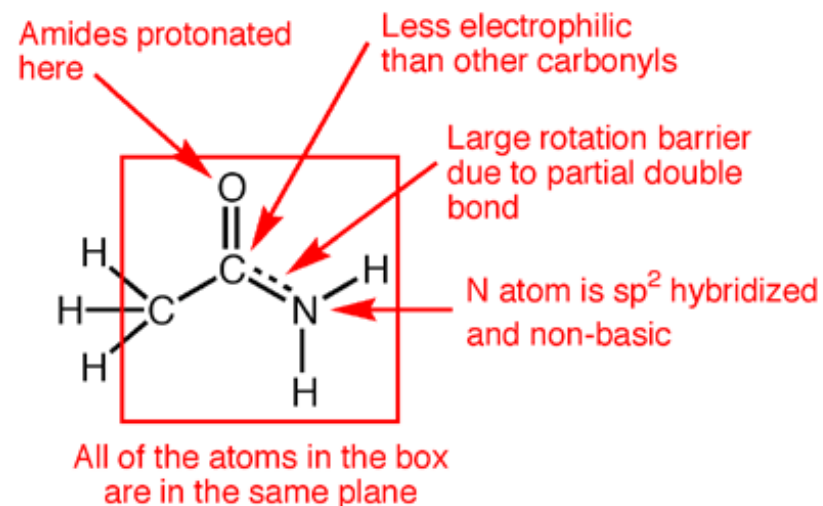
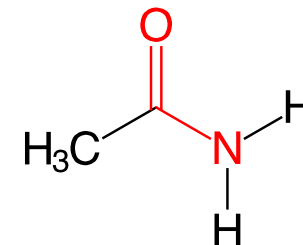
Amides

- ▶ **Amides** are derivatives of carboxylic acids in which a nitrogen group ($-\text{NH}_2$) replaces the hydroxyl ($-\text{OH}$) group of carboxylic acids.
- ▶ They contain the carboxamide functional group ($-\text{CON}-$).
 - ▶ This group is also called an amino carboxyl or sometimes just amide.
- ▶ Nitrogens in carboxyamides look like they should be sp^3 (tetrahedral), like amines.
 - ▶ But they're not.
 - ▶ Because of resonance, they have a sp^2 (trigonal planar) geometry.



Amides

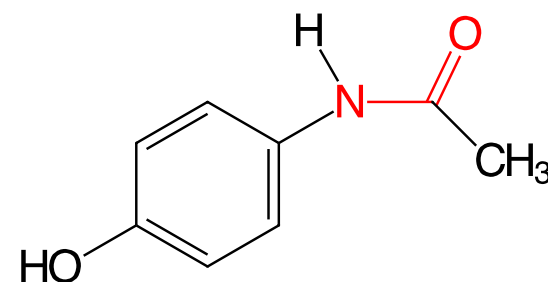
- ▶ Amide and ester structure is more different than you might think.
- ▶ This delocalization has several important consequences for amide groups.
 - ▶ There is a partial double bond between the carbonyl carbon atom and the nitrogen atom of the amide.
 - ▶ The nitrogen atom is sp^2 hybridized, because otherwise you could not have the 2p orbital to take part in the pi electron delocalization.
 - ▶ The entire amide group is planar.
 - ▶ The carbonyl carbon atom is much less reactive as an electrophile compared to other carboxylic acid derivatives.
 - ▶ Since the C-N bond of an amide cannot rotate freely (partial double bond) you can have "cis" and "trans" amides.



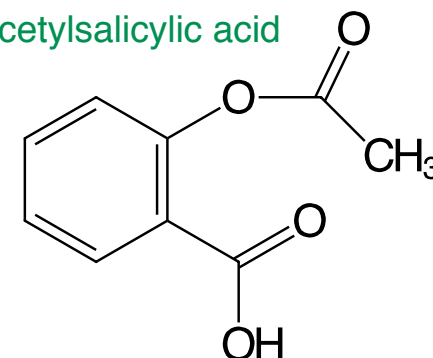
Amides

- ▶ Acetaminophen, an analog of acetylsalicylic acid (aspirin), has been sold by the trade name Tylenol™ since 1955.
- ▶ It's now off patent and available as a generic.
 - ▶ Tylenol has aspirin's analgesic (pain relief) and anti-pyretic (fever reducing) properties.
 - ▶ It does not have the anti-inflammatory properties of aspirin.
 - ▶ It is less acidic than aspirin and better tolerated by many children and adults.
 - ▶ It can cause liver problems in high doses.
 - ▶ There accounts for more than 100,000 calls to poison centers, roughly 60,000 emergency-room visits and hundreds of deaths each year in the United States. In England, it is the leading cause of liver failure requiring transplants.
 - ▶ In 2009, the FDA issued guidelines for adding overdose guidelines to packages and in 2011, the agency confirmed the link between the drug and liver damage.

acetaminophen

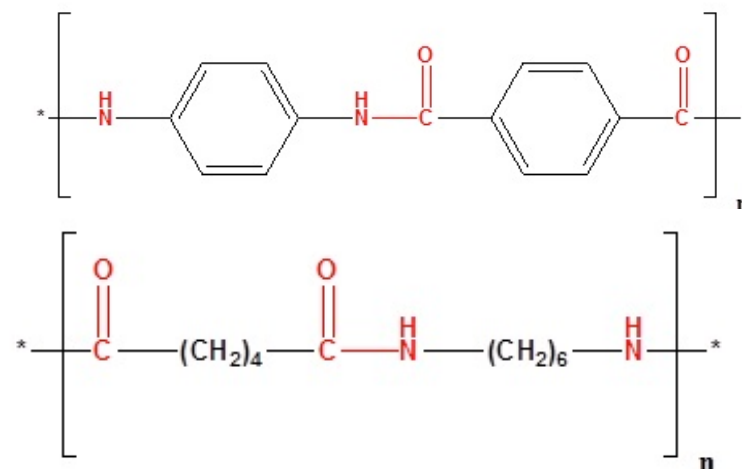


acetylsalicylic acid



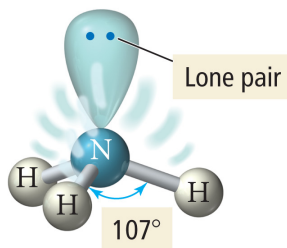
Amides

- ▶ Polymers of amides have especially strong bonds and are used to make many synthetic fibers.
- ▶ In 1931, the American chemist Wallace Hume Carothers discovered a process for making one of the first synthetic fibers by linking amides.
- ▶ He found that the addition of adipic acid to hexamethylene diamine resulted in the formation of a strong, fiber-like product to which he gave the name Nylon 66.
 - ▶ The 66 part of the name reflects the fact that adipic acid and hexamethylene diamine each contain six carbon atoms in their molecules.
- ▶ Kevlar, used in body armor, is another amide polymer.

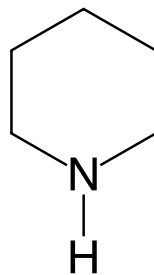
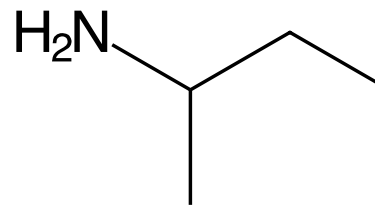
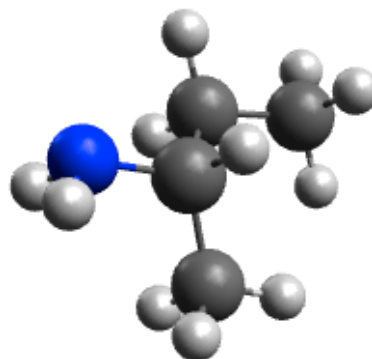
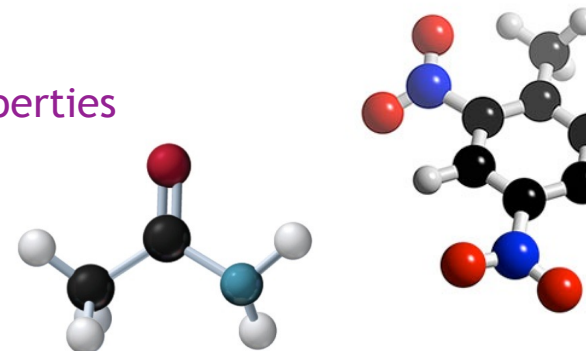


Amines & Amides

- ▶ Nitrogen
- ▶ Ammonia
 - ▶ Structure & Shape
- ▶ Amines
 - ▶ Classifications
 - ▶ Naming & Properties
 - ▶ Amines as bases/salts
 - ▶ Neutralization Rxns
 - ▶ Solubility
 - ▶ Uses
 - ▶ Heterocyclic Amines & Alkaloids



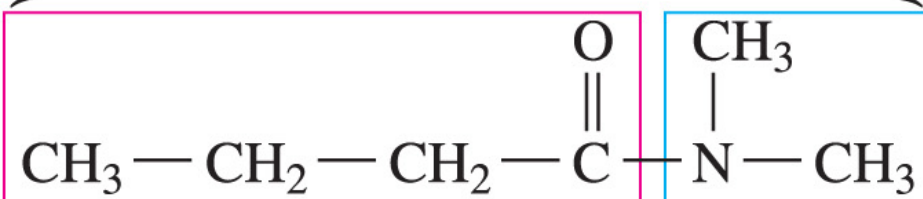
- ▶ Amides
 - ▶ Structure & Properties
 - ▶ Naming
 - ▶ Reactions
 - ▶ Amidation
 - ▶ Hydrolysis



- ▶ In both the common and IUPAC names, amides are named by dropping the oic acid (IUPAC) or ic acid (common) from the carboxylic acid name and adding the suffix **amide**.
- ▶ Alkyl groups attached to the nitrogen of an amide are named with the prefix N-, followed by the alkyl name.

From butanoic acid
(butyric acid)

From *N,N*-Dimethylamine



IUPAC
Common

N,N-Dimethylbutanamide
N,N-Dimethylbutyramide

