

2.3: Functional groups containing sp^3 -hybridized heteroatom

Learning Objectives

- Recognize and assign IUPAC name to functional groups containing sp^3 -hybridized heteroatoms, including haloalkanes, alcohols, ethers, and amines.
- Predict the polarity of the bonds in the functional groups of haloalkanes, alcohols, ethers, and amines and recognize the creative sites based on the partial charges in the functional group regions.
- Identify primary, secondary, tertiary, and quaternary designation of haloalkanes, alcohols, ethers, and amines.

Halogenated hydrocarbons

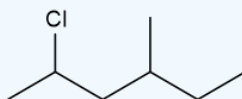
When a H in a hydrocarbon is replaced an X, where X is a halogen, i.e., fluorine (F), chlorine (Cl), bromine (Br), or iodine (I), it is a halogenated hydrocarbon. A halogenated alkane is called **haloalkane**.

Nomenclature of halogenated hydrocarbons

Halogen is treated as a branch of a hydrocarbon. The parent chain is numbers following the same rules as for branched hydrocarbons, and the halogens are listed in alphabetic order, preceded by location number, like other alkyl branches.

✓ Example 2.3.1

What is the IUPAC name of the following compound?



Solution

- The longest chain is the parent name: the longest chain is 6-C long, so the parent name is hexane.
- List the branches before the parent name in alphabetic order: the branches are chloro- and methyl-, so: chloromethylhexane
- Number the parent chain from the end that gives the lowest number to the first branch: Cl is at #2 from the right, and CH_3 is at #3 from the left, so number the parent chain from the right side that gives #2 to Cl and #4 to methyl.

Answer: 2-chloro-4-methyl hexane

✓ Example 2.3.2

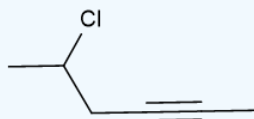
Wright the skeletal structure of 5-chlorohex-2-yne?

Solution

Find the parent name: hex-2-yne. Hex tells six C chain and 2-yne tells there is a triple bond at C#2, i.e.



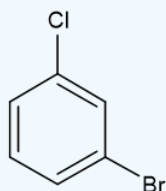
Attach the branches to the parent chain according to their location numbers: the only branch in this chase is chloro- at C#5.



Answer: 5-chlorohex-2-yne

✓ Example 2.3.3

What is the IUPAC name of the following compound?



Solution

- The longest chain is the parent name: the longest chain is 6-C cycle with alternate double bonds, i.e., all the C's are sp²-hybridized, i.e., an aromatic hydrocarbon with parent name benzene.
- List the branches before the parent name in alphabetic order: the branches are chloro- and bromo-, so: bromochlorobenzene
- Number the benzene ring starting from the 1st branch and going in the direction that gives the lowest number to the 2nd branch: Br is at #1, and Cl is at #3.

Answer: 1-bromo-3-chlorobenzene

Physical properties of halogenated hydrocarbons

The halogen atom is sp³-hybridized with three sp³ orbitals occupied by lone pairs, and one makes bonds with the C, i.e., R- \ddot{X} ·, where X is a halogen: F, Cl, Br, or I. The lone pairs are usually not shown except when needed. The C-X bond is polar, i.e., $\delta^+ \delta^-$ C-X, because halogens are more electronegative than C. It makes the C a δ^+ , i.e., an electrophile in reactivity. The lone pairs also add to the polarity because these electrons are localized on one side of the nucleus in sp³ orbitals. The bond polarity can be observed from electrostatic potential maps, shown in Table 5. Recall that green is neutral, red is δ^- and blue is δ^+ in electrostatic potential map. Note that the listed electronegativity values of C and I are the same, but the bond is still polar. This is because the listed values are slightly different from the actual values. Further, the polarizability increases in this order: F<Cl<Br<I, i.e., I is the most polarizable.

📌 What is polarizability

Polarizability is the tendency of a matter to acquire dipole-moment when subjected to an electric field. Larger atoms have more loosely held outermost electrons, which makes them more polarizable. Therefore, the polarizability increases in going from top to bottom in a group, e.g., the polarizability order of halogen is: F<Cl<Br<I.

Bond length increases in this order: F<Cl<Br<I and electronegativity has the opposite trend, i.e., decreases in this order: F>Cl>Br>I. The dipole moment depends on both the electronegativity difference of the bonded atoms and the bond length; the two effects contradict each other. As a result, the dipole moment does not change much by changing the halogen. The bond dissociation energy decrease in this order: F>Cl>Br>I, which makes C-F the strongest and the least reactive and C-I the weakest and the most reactive group.

Table 5: Physical characteristics of C-X bond in comparison with C-H bond.

Halogen	H for reference	F	Cl	Br	I
Electrostatic potential map					
C-X bond length (pm)	109	139	178	193	214

Halogen	H for reference	F	Cl	Br	I
C–X bond dissociation energy (kJ/mol)	440	464	355	309	228
Electronegativity of X or H	2.2	4.0	3.0	2.8	2.5
Dipole moment (D)	0.33	1.85	1.87	1.81	1.62

Solubility in water and boiling points of fluoro- and chloro-alkanes are comparable to alkanes of the same molar mass. Although the C–F and C–Cl are polar that tend to increase intermolecular forces due to dipole-dipole interaction, the volume of the molecule is small compared to the alkane of similar molar mass due to F or Cl being heavier atoms. Smaller volume means less contact area and fewer intermolecular forces. The opposing factors cancel each other.

Haloalkanes are denser than alkanes. Mono-fluoroalkanes and mono-chloroalkanes are less dense than water, but bromo- and iodo-alkanes are denser than water. For example, $\text{CH}_3\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{Br}$ are liquids having densities of 0.891 g/mL and 1.354 g/mL at 25 °C. Although mono-chloroalkanes are less dense than water, di-, tri-, and tetra-chloroalkanes are denser than water. For example, CH_3Cl is a gas at room temperature with a density of 1.003 g/mL at its boiling point -23.8 °C, while CH_2Cl_2 , CHCl_3 , and CCl_4 are liquids with density higher than water, i.e., 1.327 g/mL, 1.483 g/mL, and 1.594 g/mL, respectively. So, hydrocarbons float on water while the denser haloalkanes sink in water.

Some uses of halogenated hydrocarbons

C–I, C–Br, and C–Cl bond are polar and weaker than C–H that makes them reactive functional groups. The raw organic material, i.e., alkanes, is usually first converted to haloalkanes intermediates to synthesize other organic compounds. The C–F bond is stable, which is why Teflon, composed of $-(\text{CF}_2)_n-$ chains, is one of the most inert polymers. Haloalkenes with all of the C–H bonds replaced with C–F or C–Cl, called chlorofluorocarbons (CFCs) are usually nontoxic, nonflammable, odorless, and noncorrosive liquids that make them ideal as solvents, degreasing agents, and heat transfer fluids in air condition and refrigerator systems. For example, CCl_2F_2 (Freon-12) and CCl_3F (Freon-11) were used as refrigerants, and CCl_4 common name carbon tetrachloride was used as a solvent, cleaning and degreasing agent. They are being phased out because Freons destroy the stratosphere's ozone layer, and CCl_4 is toxic and carcinogenic.

Role of CFCs in the ozone hole

The CFCs like CCl_2F_2 and CCl_3F , being stable molecules, survive when released in the atmosphere, reach the stratosphere, and decompose when UV light shines on them in the stratosphere. Their by-products, particularly Cl_2 , catalyze the destruction of the ozone layer in the stratosphere that filters out UV light. It resulted in an ozone-depleted region over the southern hemisphere called the ozone hole. Without the ozone layer, UV light reaches the earth's surface and causes damage to living things. Therefore, the CFCs are being replaced with haloalkanes with some C–H bonds left to make them less stable, so they may decompose before reaching the stratosphere. As a result of this worldwide effort, the ozone hole is recovering over time, as shown in Figure 2.3.1.

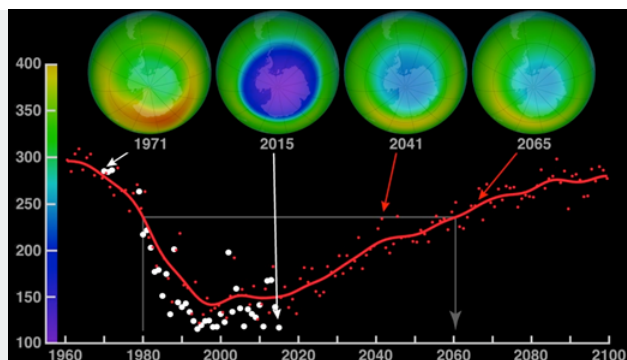


Figure 2.3.1: Ozone hole recovery projection, 1960-2100, the x-axis is time in years, and the y-axis shows the ozone concentration in Dobson units, where purple is the lowest and reddish is the highest concentration ratio. (Copyright; NASA, Public domain, via Wikimedia Commons)

The most promising replacements include hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), like $\text{CF}_3-\text{CH}_2\text{F}$ called HFC-134a and $\text{CH}_3-\text{CCl}_2\text{F}$ called HCFC-141b. Carbon tetrachloride CCl_4 , which is toxic and carcinogenic, is also being replaced with dichloromethane CH_2Cl_2 solvent.

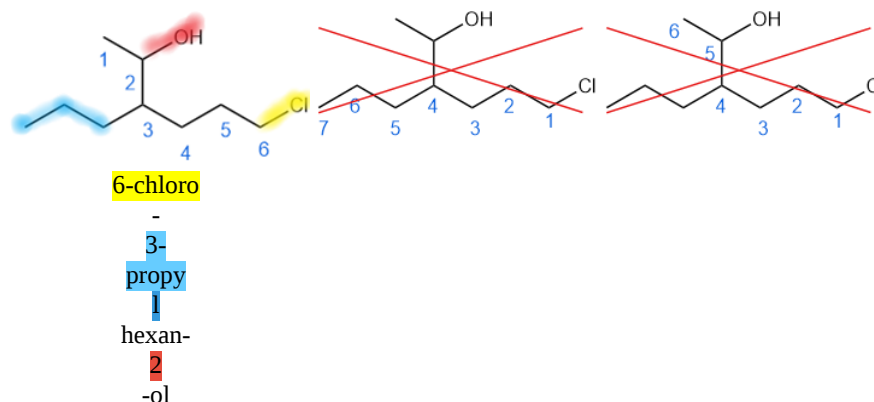
Alcohols

An alkyl group attached with an alcohol ($-\text{OH}$) group, i.e., $\text{R}-\text{OH}$, is an alcohol. A benzene ring attached with an alcohol group is a phenol.

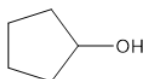
Nomenclature of alcohols and phenols

The nomenclature of hydrocarbons is followed for IUPAC names of alcohols and phenols with the following changes.

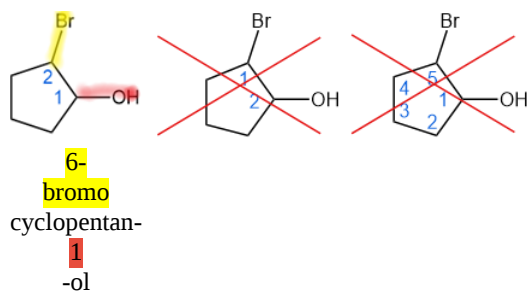
- The longest chain containing the $-\text{OH}$ group is chosen for the parent name, and the 'e' in the suffix -ane, -ene, or -yne is replaced with -ol. For example, CH_3-OH is methanol, and $\text{CH}_3\text{CH}_2-\text{OH}$ is ethanol.
- Numbering starts from the end, giving the $-\text{OH}$ group the lowest number in preference over hydrocarbon or halogen branches. This is demonstrated in the following example, where the parent chain is not heptane; it is hexane that contains $-\text{OH}$ group, and the number starts from the end that gives $-\text{OH}$ lowest number 2 not from the other end that gives $-\text{Cl}$ the lowest number 1.



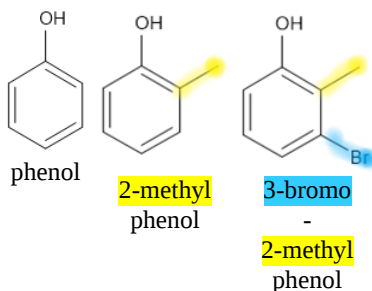
- In a cyclic compound containing only $-\text{OH}$ group, numbering is not needed, e.g., number is not used in naming cyclohexanone:



- In a cyclic compound containing $-\text{OH}$ group and a hydrocarbon or halogen group, numbering begins from $-\text{OH}$ group, e.g.:

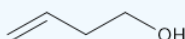


- A benzene ring containing an —OH group is given the parent name phenol. If there is another group present, the numbering starts from the —OH group, and phenol is used as the parent name, e.g.:



✓ Example 2.3.1

What is the IUPAC name of this compound?



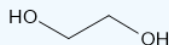
Solution

- Find the parent name: four C chain is but, and double bond makes it an alkene, i.e., butene.
- Change the 'e' of the suffix with -ol that tells it is an alcohol, i.e., butenol.
- Start number from the end that gives —OH group the lowest number: —OH receives #1 and $\text{C}=\text{C}$ receives #3.

Answer: but-3-en-1-ol

✓ Example 2.3.2

What is the IUPAC name of the following alcohol?



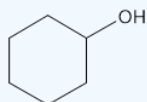
Solution

- Find the parent name: two C chain is ethane.
- Replace the last 'e' of the suffix with -ol, which tells it is an alcohol; in this case, there are two —OH groups, so add di, i.e., ethandiol
- The number is the same from either end, i.e., #1 and #2 for the two —OH groups.

Answer: ethane-1,2-diol

Ethane-1,2-diol () is known by its common name ethylene glycol. Similarly, propane-1,2,3-triol () is known by its common name, glycerol or glycerine.

✓ Example 2.3.3



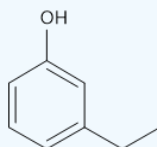
What is the IUPAC name of this compound?

Solution

- Find the parent name: six C cycle is cyclohexane.
- Replace the last 'e' of the suffix with -ol which means it is an alcohol, i.e., cyclohexanol.
- A cycle with only -OH group do not need numbering.

Answer: cyclohexanol

✓ Example 2.3.4



What is the IUPAC name of this compound?

Solution

- Find the parent name: six C chain with all sp^2 -hybridized C's is benzene, and benzene with an -OH group is phenol.
- List the substituent other than OH as prefix: ethylphenol.
- Start numbering from the -OH group and continue in the direction that gives the lowest overall number to the other substituents: ethyl receives #3.

Answer: 3-ethylphenol

Physical properties of alcohol and phenols

Alcohols contain a sp^3 -hybridized O bonded to a C and a H and the remaining two sp^3 -orbitals occupied by lone pairs, i.e.,: $R-\ddot{O}-H$. The O atom is more electronegative than C and H, which means both the bonds are polar, i.e., $\overset{\delta+}{C}-\overset{\delta-}{O}-\overset{\delta+}{H}$, as observed in the electrostatic maps of some alcohols in Figure 2.3.2.

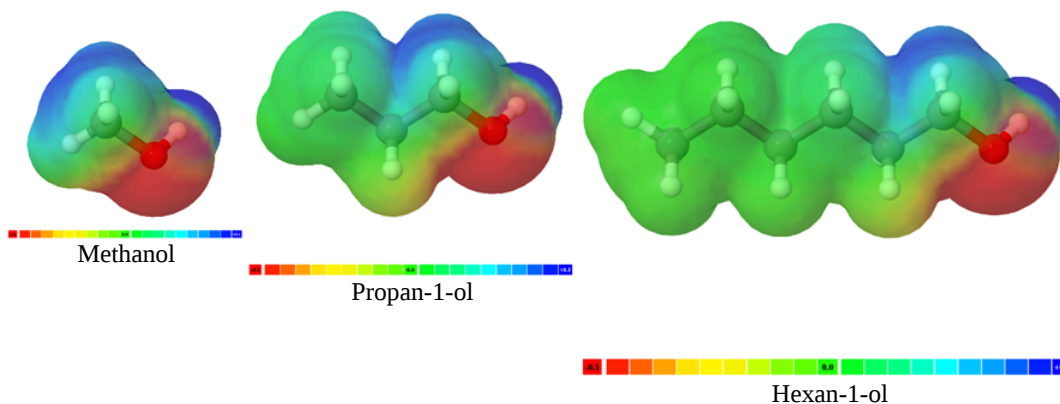


Figure 2.3.2: Electrostatic potential map of three alcohol examples, where O is red, H is white, and C is gray in the model spheres inside the electron cloud. δ^- on O (red color), δ^+ on C (blue color), and δ^- on H (blue color), and neutral on the alkyl chain (green color) can be observed. (Copyright; public domain).

An alcohol group has three reactive points: an electrophilic $\overset{\delta+}{C}$, an acidic $\overset{\delta+}{H}$, and nucleophilic/basic $\overset{\delta-}{O}$. The acidity of an alcoholic H is obvious from the fact that it has a $pK_a \sim 16$ that is about the same acid strength as H_2O .

📌 Nucleophile/base and electrophile/acid?

Recall that δ^+ C is called an electrophile. At the same time, proton exchange reactions are acid/base reactions, i.e., δ^+ H is an acidic proton, and a δ^- site when reacts with a C is called nucleophile, and when it donates its lone pair to a H, it is called a base.

Alcohols have significantly higher boiling points compared to alkanes of comparable molar mass.

For example, the boiling point of methanol (molar mass 32 g/mol) is 65 °C which is significantly higher than the -89 °C boiling point of ethane of comparable molar mass (30 g/mol). It is explained by the fact that, in addition to London dispersion forces, alcohols have hydrogen bonding between H of one molecule with O of the neighboring molecule as illustrated in Figure 2.3.3. It takes more thermal energy to break London dispersion forces + hydrogen bonding in alcohols than London dispersion forces alone in alkanes. The boiling points of alcohols increase as their molar mass increases, as shown in Table 6.

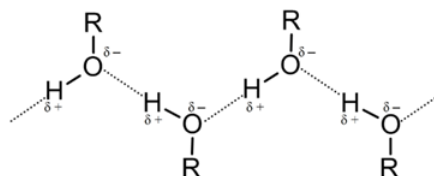


Figure 2.3.3: Illustration of hydrogen bonding in alcohol. (Copyright; Secalinum, Public domain via Wikimedia Commons)

Smaller alcohols having up to three C' are entirely soluble in water, i.e., miscible, one with four C' is partially soluble, and those with longer than four C' are almost insoluble as listed in Table 6. This trend of water solubility change is explained by a balance between hydrophilic and hydrophobic components in an alcohol molecule, explained later.

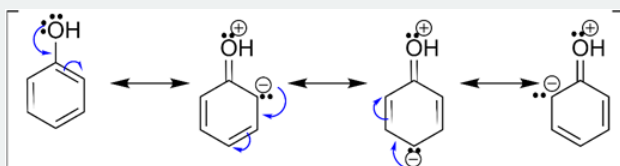
Table 6: Molecular weight, boiling points, and solubility in water of some alcohols

IUPAC name	Molecular formula	Molecular weight (g/mol)	Boiling point (°C)	Solubility in water
Methanol	CH ₃ OH	32	65	Miscible
Ethanol	CH ₃ CH ₂ OH	46	78	Miscible
Propan-1-ol	CH ₃ CH ₂ CH ₂ OH	60	97	Miscible
Butan-1-ol	CH ₃ CH ₂ CH ₂ CH ₂ OH	74	117	Slightly soluble
Pentan-1-ol	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	88	138	Insoluble
Hexan-1-ol	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH	100	157	Insoluble

Phenol has an -OH attached to an sp²-hybridized C of a benzene ring. Phenol is a volatile white crystalline solid that melts at 41 °C, and boils at 182 °C. Phenol is partially soluble in water.

📌 -OH -An activating group on a benzene ring

When an atom with a lone pair of electrons on it is bonded to an sp²-hybridized C, it changes its hybridization from sp³ to sp² for resonance to happen. The driving force is the resonance stabilization effect. The same happens to O in phenol resulting in resonance that sends electrons from O into the benzene ring as illustrated below. Consequently, the benzene ring of phenol is more electron-rich, i.e., more nucleophilic than benzene without such a group attached. The groups like -OH that enhance the reactivity of the benzene ring by donating electrons to the ring are called **activating groups**.



Another consequence of this electron donation by O is that the O is more able to hold on to the electrons of O–H bond when the proton leaves acting as an acid, i.e., phenolic O–H is a stronger acid ($pK_a \sim 10$) compared to an alcoholic O–H ($pK_a \sim 16$).

The balance between the hydrophilic and hydrophobic character of organic compounds containing a polar group

Polar functional groups like –OH are attracted to water, i.e., water-loving or **hydrophilic**. This is based on the general principle "like dissolves like." On the other hand, Alkyl groups are nonpolar and repel water molecules, i.e., **hydrophobic**. Alkyl groups are more soluble in lipids and fats, which are also called **lipophilic or nonpolar**. Alcohols have both groups in them, and their properties depend on which group dominates. The hydrophilic character dominates when the alkyl chain is small, three (C's or small, and the hydrophobic character dominates when the alkyl chain is long, i.e., more than four (C's long making the compound slightly soluble or insoluble. In summary,

- increasing the alkyl-group increases hydrophobic character, e.g., propan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) is water soluble, but butan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) is partially soluble, and
- increasing the polar group increases the hydrophilic character, e.g., butan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) with one (–OH) group is partially soluble in water, but butane-1,2-diol ($\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$) with two (–OH) groups is soluble.

This trend is generally applicable to all polar groups containing organic compounds.

Some examples of important alcohols and phenols

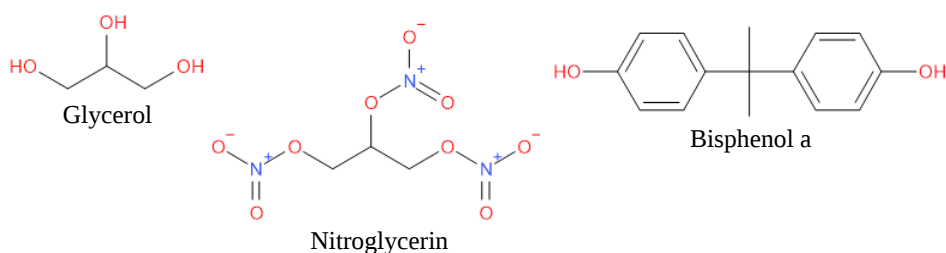
Methanol ($\text{CH}_3\text{–OH}$) is used as a solvent, paint remover, and fuel and converted to formaldehyde which is then used to make plastics. If methanol is ingested, it converts to formaldehyde, which causes headache and blindness and may cause death. That is why methanol is mixed with ethanol not meant for drinking.

Ethanol ($\text{CH}_3\text{–OH}$) is the active ingredient in alcoholic beverages. It is also used as a solvent for perfumes, varnishes, and medicines, e.g., in tincture iodine. The fermentation process obtains ethanol, but these days, it is mainly derived from ethene.

Isopropanol. 2-methylpropanol, commonly known as isopropanol, kills bacteria and viruses. Ethanol also has the same property. Ethanol or isopropanol are 60% to 80% fraction of hand sanitizers; the remaining is usually ethylene or glycerin to keep the skin soft. If ethanol is the active ingredient in the hand sanitizer, care is needed as ethanol is volatile and flammable.

Ethylene glycol, i.e., ethane-1,2-diol ($\text{HO–CH}_2\text{CH}_2\text{–OH}$) is used as antifreeze in cooling systems of vehicles and as a solvent for paints, inks, and plastics. Ethylene glycol is poisonous because, if ingested, it converts to oxalic acid, which causes kidney stones.

Glycerin or glycerol, i.e., propane-1,2,3-triol ($\text{HO–CH}_2\text{CH}(\text{OH})\text{CH}_2\text{–OH}$) is obtained as a byproduct during the soap making from fats and oils. It is a viscous liquid used in skin lotions, cosmetics, shaving creams, and liquid soaps. Nitroglycerin, the active component of explosive dynamite, is derived from glycerol.





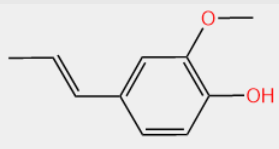
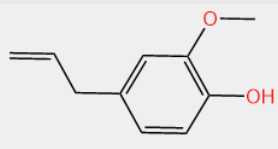
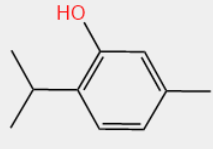
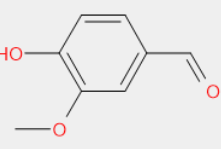


Bisphenol a (BPA) is used used in making polycarbonate that is used to manufacture beverage bottles. There is a concern that leaching out BPA from beverage bottles may cause harmful health effects.

Phenol is primarily used for the production of precursors of plastics. Phenol is used as an antiseptic and disinfectant. Phenol is also a part of the structure of essential oils responsible for plants' odor and flavor, e.g., isoeugenol from nutmeg, eugenol from clover, thymol from thyme, and vanillin from vanilla, shown in Table 1.

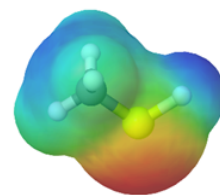
Table 3: Examples of phenol present in essential oils

Isoeugenol from nutmeg	Eugenol from clover	Thymol from thyme	Vanillin from vanilla
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Isoeugenol from nutmeg	Eugenol from clover	Thymol from thyme	Vanillin from vanilla
			
			
Isoeugenol	Eugenol	Thymol	Vanillin

Thiol

Thiols are sulfur analogs of alcohols, i.e., they contain the thiol ($-\text{SH}$) group. Like alcohols, thiols contain an electrophilic C and acidic H attached to S atom as illustrated by the electrostatic potential map of methanethiol CH_3-SH in the figure on the right, where S is shown as yellow, H as white, and C as gray sphere in the model.



The thiols are named following the rules of alcohols, except that suffix -thiol is added to the name of alkane, e.g., CH_3-SH is methanethiol and $(\text{CH}_3\text{CH}_2-\text{SH})$ is ethanethiol.

One characteristic of thiols is that they have a strong odor, e.g., methanethiol (CH_3-SH) is an odor-causing compound present in oysters, cheddar cheese, onions, and garlic. The garlic odor also contains prop-2-ene-1-thiol ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{SH}$). Onion odor is also due to propane-1-thiol ($\text{CH}_3\text{CH}_2\text{CH}_2-\text{SH}$), which is a lachrymator, i.e., a substance that makes eyes tear.

Ethers

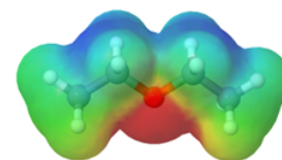
Ethers have O with two single bonds with two alkyl groups, i.e., $\text{R}-\text{O}-\text{R}'$ group.

Nomenclature of ethers

IUPAC naming of ether follows the rules of branched alkanes. The large alkyl group is named as parent chain, and the smaller alkyl groups with oxygen are named as a branch, i.e., an alkoxy ($\text{R}-\text{O}-$) group. For example, $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$ is ethoxyethane and $\text{CH}_3\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$ is 1-methoxypropane. However, trivial names for ethers are often used. A common name is formed by listing the two alkyl groups in alphabetic order, followed by the word ether. For example, common name of $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$ is diethylether and of $\text{CH}_3\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$ is propyl methyl ether.

Physical properties of ethers

Ethers contain a sp^3 -hybridized O bonded to two C's and the remaining two sp^3 -orbitals occupied by lone pairs, i.e.,: $\text{R}-\ddot{\text{O}}-\text{R}$. The O atom is more electronegative than C, which means both the bonds are polar, i.e., $\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{C}}$, as observed in the electrostatic maps of diethylether shown on in figure on the right.



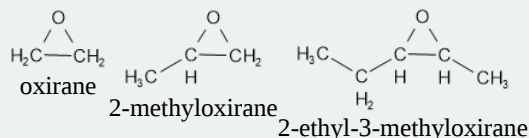
Since there is no $\text{O}-\text{H}$ bond, pure ethers do not have hydrogen bonding; they have a weak dipole-dipole interaction and London dispersion forces. Therefore, the boiling points of ether are comparable to alkanes of the same molecular mass, e.g., diethyl ether (molar mass 74 g/mol) has a boiling point of 35°C , which is almost the same as the boiling point of pentane (molar mass 72 g/mol, boiling point 36°C). However, ethers do have $\overset{\delta-}{\text{O}}$ and that can establish hydrogen bonding with $\overset{\delta+}{\text{H}}$ of water molecule. So, ethers have solubility in water comparable to alcohols of the same

molar mass, i.e., ethers with three or less C's are miscible in water, and those with four or more C's are slightly soluble or insoluble in water.

Ethers are less reactive than alcohols because alcohols have an acidic $\overset{\delta+}{\text{H}}$, which is missing in ethers. Because of relatively low chemical reactivity, ethers are used as solvents to conduct other compounds' reactions.

📌 Epoxides -reactive ethers and sterilizing agents

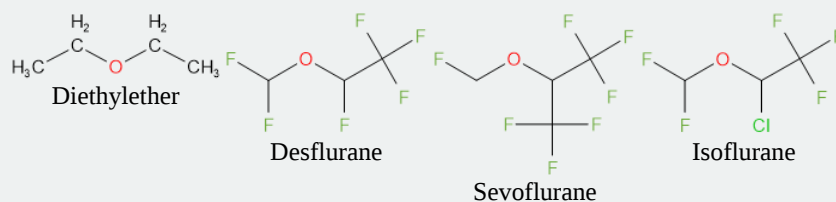
Epoxides are cyclic ethers in which one atom in a three-membered ring is O. Epoxides take the parent name oxirane, and numbering, if needed, starts from the O atom. Three examples are shown below.



Epoxides are unstable and highly reactive due to angle strain as the bonds bent from a regular angle of 109.5° to 60° . They are used as intermediates in organic synthesis. Oxirane is a room-temperature gas that reacts fast with the compounds in microorganisms, causing their death. So, it is used as a fumigant in foodstuffs and textiles and as a hospital sterilizer for surgical instruments.

📌 Ethers as anesthetics

Diethyl ether has been used as an anesthetic agent for a long time. Its use in anesthesia has been discontinued because it is a volatile and flammable gas posing a fire or explosion risk in the surgery room. Further, it has an irritating effect on the respiratory passages and causes nausea. Fluorinated or chlorofluorinated ethers, such as desflurane, sevoflurane, and isoflurane listed below, are used as anesthetic agents because they are less volatile, less flammable, and have fewer other undesirable side effects.



Peroxides, sulfides, and disulfides

Peroxides have O—O bond, which is one of the weak bonds with bond dissociation energy ~ 200 kJ/mol, about half of the strength of a C—C or a C—H bond. This bond is found in **hydroperoxy group** ($\text{R}-\text{O}-\text{O}-\text{H}$) and **peroxy group** ($\text{R}-\text{O}-\text{O}-\text{R}'$). The peroxides are less common but more reactive due to weak O—O bond.

Sulfides are S analogs of ethers, i.e, they have sulfide ($\text{R}-\ddot{\text{S}}-\text{R}$) group. The names of sulfides are similar to those of ethers, i.e., list the two alkyl groups alphabetically, followed by the word sulfide. For example, $\text{CH}_3\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_3$ is diethyl sulfide and $\text{CH}_3\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_3$ is propyl methyl sulfide. Sulfides are less common in nature. **Disulfide** $\text{R}-\text{S}-\text{S}-\text{R}$ group, i.e., a sulfur analog of peroxides found in proteins. The S—S is a relatively weak bond with a bond dissociation energy of ~ 250 kJ/mol.

Primary (p), secondary (s), tertiary (t), and quaternary classification

The p, s, t- classification of C's and H's

In an organic compound:

- if a C is not bonded with any other C or bonded with only one other C, it is a **primary C**;
- if bonded with two other C's, it is a **secondary C**;
- if bonded with three other C's, it is a **tertiary C**; and
- if bonded with four other C's, it is a **quaternary C**.

The H's on a primary C's are **primary** H's, those on a secondary C's are **secondary** H's, and those on tertiary C's are tertiary H's. Quaternary C's do not have any H on them. The figure on the right illustrates the primary, secondary, tertiary, and quaternary C's and H's marked in different colors and pointed by arrows. Table 1 illustrates the primary, secondary, and tertiary haloalkanes, alcohols, alkyl groups in ethers, and amine.

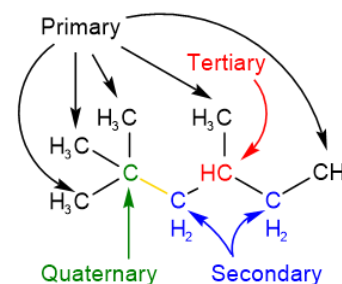


Table 1: Primary, secondary, and tertiary classifications of haloalkanes, alcohols, alkyl groups, and amines.

(Common names using secondary (s) and tertiary (t) designation or *iso* (for the case of secondary propyl) alkyl groups are used.)

Classification	Primary	Secondary	Tertiary
Haloalkanes	$\begin{array}{c} \text{H}_2 \\ \\ \text{H}_3\text{C}-\text{C}-\text{Cl} \end{array}$ ethyl chloride	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{H}-\text{Cl} \end{array}$ isopropyl chloride	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{Cl} \\ \\ \text{H}_3\text{C} \end{array}$ <i>t</i> -butyl chloride
Alcohols	$\begin{array}{c} \text{H}_2 \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \end{array}$ ethanol	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{H}_2 \end{array}$ <i>sec</i> -butanol	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\ \\ \text{H}_3\text{C} \end{array}$ <i>t</i> -butanol
Alkyl groups in ethers	$\begin{array}{c} \text{H}_2 \quad \text{H}_2 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{C}-\text{CH}_3 \\ \quad \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array}$ diethyl ether	$\begin{array}{c} \text{H}_3\text{C} \quad \text{H}_3\text{C} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{CH}-\text{CH}_3 \\ \quad \\ \text{H} \quad \text{H}_2 \end{array}$ diisopropyl ether	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{C}-\text{CH}_3 \\ \quad \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array}$ ditertiary butyl ether
Amines	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{NH}_2 \\ \\ \text{H}_3\text{C} \end{array}$ <i>t</i> -butyl amine	$\begin{array}{c} \text{H}_2 \\ \\ \text{H}_3\text{C}-\text{C}-\text{N}-\text{CH}_3 \\ \\ \text{H} \end{array}$ ethyl(methyl)amine	$\begin{array}{c} \text{H}_2 \quad \text{H}_2 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{N}-\text{C}-\text{CH}_3 \\ \quad \quad \\ \text{H}_2 \quad \text{H}_3\text{C} \end{array}$ ethyl(methyl)propylamine

The *p*, *s*, *t*-classification of haloalkanes and alcohols

A halogen or an –OH group:

- if bonded with a primary C, it is a **primary haloalkane**, or **primary alcohol**;
- if bonded with a secondary C, it is a **secondary haloalkane** or **secondary alcohol**;
- if bonded with a tertiary C, it is a **tertiary haloalkane** or **tertiary alcohol**.

Quaternary C's do not have any halogen or –OH group on them.

The *p*, *s*, *t*-classification of alkyl groups

An alkyl group connected through:

- a primary C to a parent chain or a functional group is a **primary alkyl group (p-alkyl)**;
- a secondary C is a **secondary alkyl group (s-alkyl)**; and
- a tertiary C is a **tertiary alkyl group (t-alkyl)**.

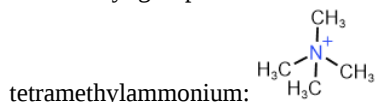
The primary (*p*), secondary (*sec*, or *s*), and tertiary (*t*) designation of alkyl groups (except for *isopropyl* used in the place of *sec-propyl*) are also accepted in IUPAC nomenclature, and these designations are often used in common names of organic compounds,

as shown by the commons in Table 1.

The *p*, *s*, *t*-classification of amines

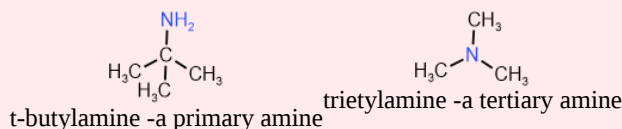
Amines are organic compounds that have one or more H's of ammonia (NH₃) replaced with an aliphatic hydrocarbon group.

- If there is only one alkyl group bonded with the N, it is a **primary amine group**, i.e., RNH₂;
- if two alkyl groups are bonded with the N, it is a secondary amine group, i.e., RR'NH;
- if three alkyl groups are bonded with the N, it is a **tertiary amine group**, i.e., RR'R''N, and
- if four alkyl groups are bonded with the N, it is not an amine but an ammonium ion, i.e., RR'R''R'''N⁺, e.g.,



Caution-*p*, *s*, or *t* designation of amines is based on the N not on the C

Unlike haloalkenes and alcohols, the primary, secondary, and tertiary classification of amines is based on whether there are one, two, or three alkyl groups bonded with the N, irrespective of the C bonded with the N is primary, secondary, or tertiary. For example, as shown below, *t*-butylamine is a primary, and trimethylamine is a tertiary amine.



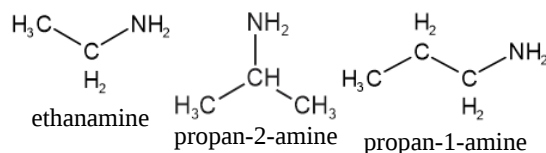
Amines

Ammonia has an sp³-hybridized N having three single bonds with nitrogen and one lone pair, i.e., :NH₃. If one or more H's of ammonia are replaced with an aliphatic hydrocarbon, it is an amine group, and the compound is an amine, i.e., RNH₂, RR'NH, or RR'R''N are amine groups. If one or more H's of ammonia are replaced with a benzene ring, it is an aromatic amine.

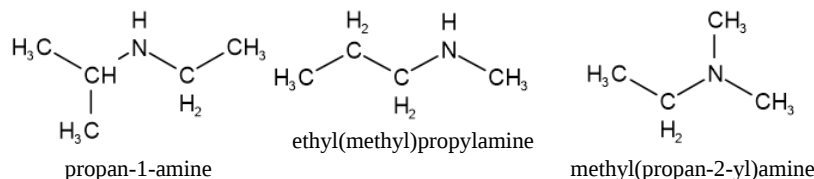
Nomenclature of amines

IUPAC naming of amines follows the rules for naming alcohols with the following changes:

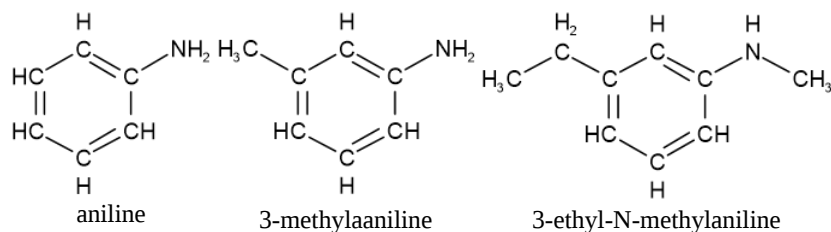
- The suffix's last letter 'e' is replaced with amine, e.g., CH₃NH₂ is methanamine. A few examples are the following.



- If more than one hydrocarbon group is attached with the N, the longest one is chosen as the parent name, and the smaller ones are listed alphabetically as substituents preceded by N-, where N tells the branch is attached to N. For example, CH₃CH₂NHCH₃ is N-methylethanamine.
- An alternate and easier way is to list the alkyl groups as substituents in alphabetic order (the middle one is enclosed in small brackets for easy reading), followed by the word amine. For example, CH₃CH₂NHCH₃ can be named ethyl(methyl)amine. A few examples are listed below.



- A benzene ring containing an -NH₂ group is given the parent name aniline. If there is another group present, the numbering starts from the -NH₂ group, and aniline is used as the parent name, e.g.:

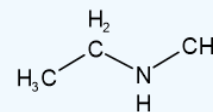


✓ Example 2.3.1

What is the IUPAC name of the compound shown in the figure on the right?

Solution

1. List the alkyl groups in alphabetic order (place the middle name in brackets) and end with the word amine: ethyl(methyl)amine, or
2. Choose the longest substituted as the parent name and the other as substitute preceded by N- to indicate the substituent is on N, i.e.,: N-methylethanamine.

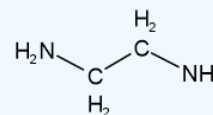


✓ Example 2.3.2

What is the IUPAC name of the compound shown in the figure on the right?

Solution

Ethane is the only alkyl group, so the stem name is ethane. It has two amine groups, so use di- preceded by number to tell the location of the amine groups: ethan-1,2-diamine.

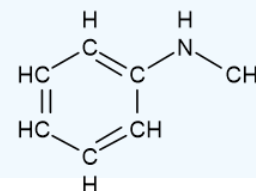


✓ Example 2.3.3

What is the IUPAC name of the compound shown in the figure on the right?

Solution

A benzene ring attached to an amine group has the parent name aniline. Methyl substituent is on N, so list it as a prefix branch name preceded by N-, i.e., N-methylaniline.

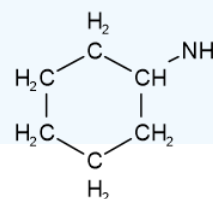


✓ Example 2.3.4

What is the IUPAC name of the compound shown in the figure on the right?

Solution

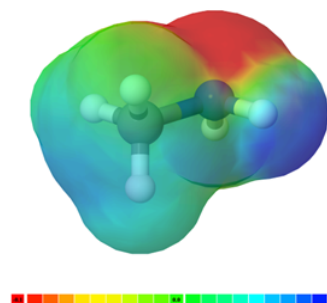
The alkyl group is cyclohexane; replace the last 'e' with amine: cyclohexanamine.



Physical properties of amines

Amines contain a sp³-hybridized N bonded to C's and H's and one sp³-orbitals occupied by lone pairs, i.e.,: RR'R'N:. The N atom is more electronegative than C, which means the C–N and N–H bonds are polar, i.e., $\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{N}}-\overset{\delta+}{\text{H}}$, as observed in the electrostatic maps of methanamine shown in the figure on the right, where N is blue, C is gray, and H is a white sphere.

The N atom is less electronegative than O, so the C–N bond (3.0-2.1 = 0.9) is less polar and less reactive than C–O (3.5-2.1 = 1.4). Due to the less electronegativity of N, it is more willing to donate its lone pair to any proton around, i.e., amines are basic compounds. Amines are also classified as organic bases.



Primary and secondary amines have hydrogen bonding, but the N—H bond is less polar than the O—H bond. Therefore, the boiling points of primary and secondary amines are higher than alkanes but lower than alcohol of comparable molar mass, as shown in Table 8.

Table 8: Molar masses and boiling points of some amines

Name	Condensed	Molar mass	Boiling point
Ethane	CH_3CH_3	30.1 g/mol	-88.6 °C
Methylamine	CH_3NH_2	31.1 g/mol	-6.3 °C
Methanol	CH_3OH	32.0 g/mol	65.0 °C
Butane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	58 g/mole	0 °C
Trimethylamine	$(\text{CH}_3)_3\text{N}$	59 g/mole	3 °C
Propylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	59 g/mol	48.0 °C

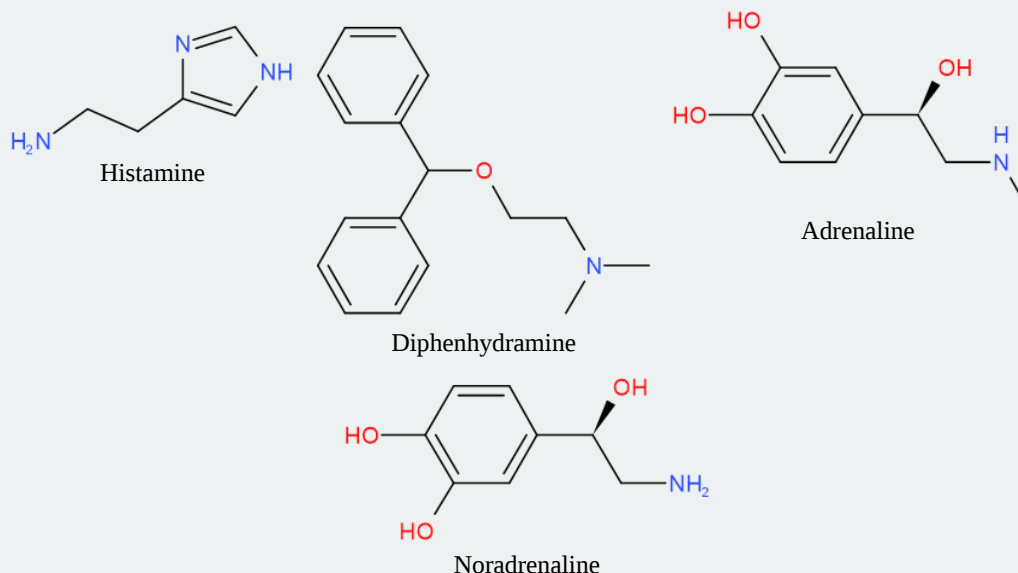
Tertiary amines have boiling points comparable with alkanes as they do not have N—H bond and do not make hydrogen bonding with each other, as shown in Table 8.

The primary, secondary, and tertiary amines make a hydrogen bonds with water. Therefore, amines containing up to five C's are soluble in water, and those with more than five C's are slightly soluble or insoluble.

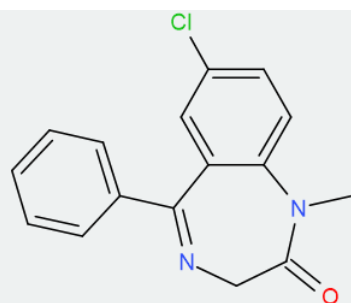
Importance of amines in health and medicine

Amines are present in amino acids, the building blocks of proteins. Amines are present in several physiologically active compounds. The body releases the histamine in response to injury or allergic reactions. Histamine causes blood vessels to dilate, and redness and swelling occur in the area. Antihistamine administered to block the effects of histamine is another amine, diphenhydramine.

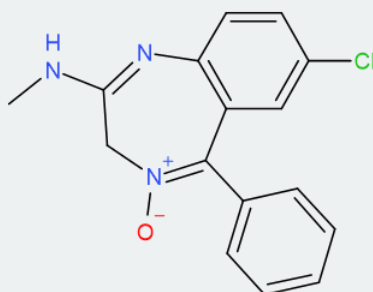
Epinephrine (adrenaline) and norepinephrine (noradrenaline) are released in a "fight-or-flight" situation. They increase blood glucose and move the blood to the muscles. Norepinephrine is a remedy for colds, hay fever, and asthma. It contracts the capillaries in the mucous membranes of the respiratory passage.



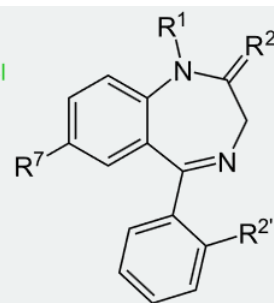
Tranquilizers are drugs that relieve the symptoms of anxiety and tension. These include diazepam (earlier name valium), Chlordiazepoxide (trade name Librium), and other benzodiazepines, which are sedative and hypnotic medicines that cause calming effects and drowsiness.



Diazepam (Valium)



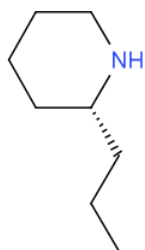
Chlordiazepoxide (Librium)



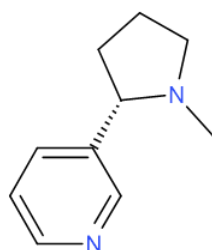
Benzodiazepines

Alkaloids

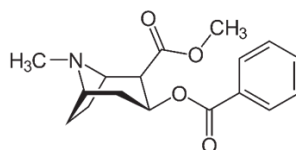
Amines can donate a lone pair to a proton relatively easily because N is less electronegative than O, i.e., amines are basic compounds with pKa value ~10. Alkaloids are nitrogen-containing basic compounds extracted from plants. Most alkaloids are physiologically active and used in anesthetics, antidepressants, and stimulants; many are habit-forming. For example, coniine extracted from "poison hemlock" can cause weakness, fast respiration, paralysis, and death. Nicotine found in tobacco is addictive, but in large doses, it causes depression, nausea, vomiting, or death. The solution of nicotine in water is used as an insecticide. Cocaine extracted from the coca plant is a stimulant for the central nervous system. Piperidine is responsible for the pungent smell and taste of black pepper. The Chemical structures of these alkaloids are shown below.



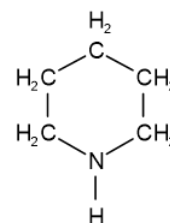
(S)-Conine



Nicotine



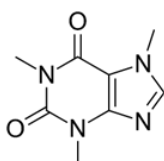
Cocaine



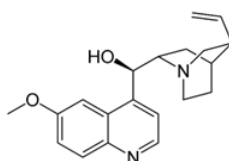
Piperidine



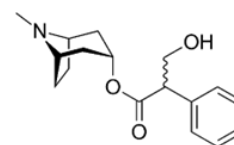
Caffeine is found in coffee and tea. Caffeine increases alertness and is used in some pain relievers to counter the drowsiness caused by antihistamines. Quinine from the bark of the cinchona tree is used to treat malaria. Atropine from belladonna accelerates slow heart rates and is anesthesia for eye exams. Their structures are shown below.



Caffeine



Quinine



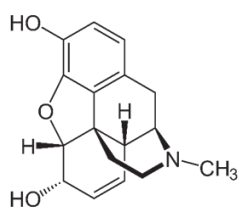
Atropine



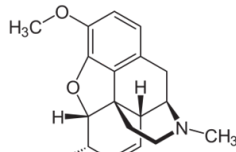
Morphine and codeine are obtained from the opium poppy plant and used as painkillers and cough syrup. Heroin, which is strongly addictive, is received by the chemical modification of morphine. OxyContin, which is a prescription drug for the relief of fever pain, is structurally similar to heroin and also has similar physiological effects. The structures of these alkaloids are shown below.



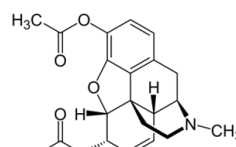
Seedhead of Opium Poppy



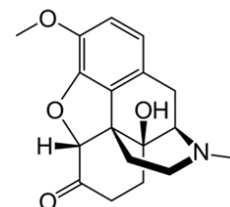
Morphine



Codeine



Heroin



OxyContin

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