Isomerism

Molecular formula: an expression that shows number and types of atoms that formed the compound.

Examples: water H_2O

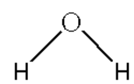
Methane CH_4

Glucose $C_6H_{12}O_6$

The molecular formula does not show how the atoms in the compound connected with each other

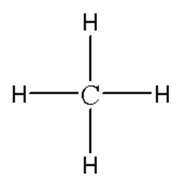
Structural formula: an expression that shows number, types of atoms that formed the compound and how these atoms connected with each other.

Water H_2O



one possible structural formula

Methane CH_4



one possible structural formula

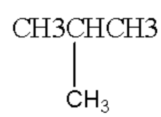
propane C_3H_8

$CH_3CH_2CH_3$

one possible structural formula

C_4H_{10}

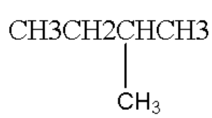
$CH_3CH_2CH_2CH_3$

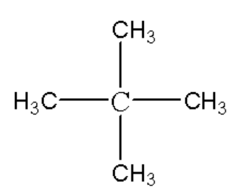


Two possible structural formulas

C_5H_{12}

CH3CH2CH2CH2CH3

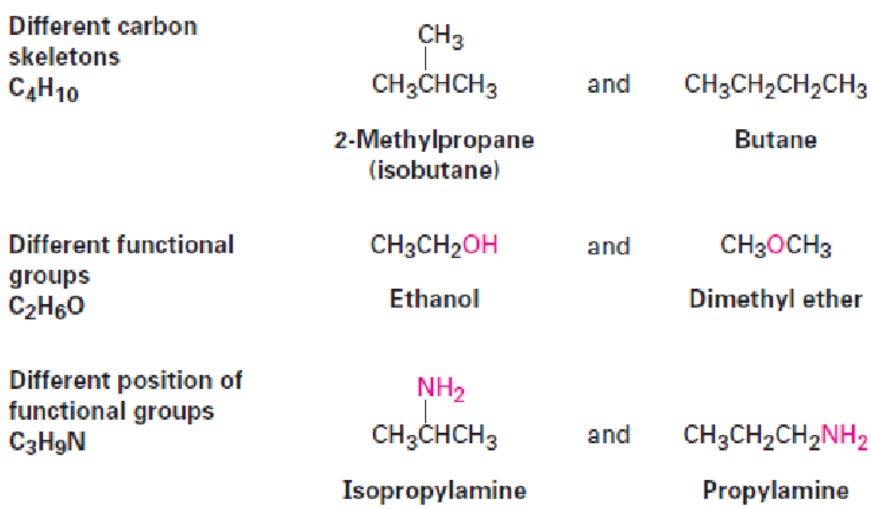




Three possible structural formulas

Compounds like the two C_4H_{10} molecules and the three C_5H_{12} molecules, which have the same formula but different structures, are called *isomers*, from the Greek *isos* + *meros*, meaning "made of the same parts." Isomers are compounds that have the same numbers and kinds of atoms but differ in the way the atoms are arranged. Compounds like butane and isobutane, whose atoms are connected differently, are called **constitutional isomers**. We'll see shortly that other kinds of isomers are also possible, even among compounds whose atoms are connected in the same order. As Table 3.2 shows, the number of possible alkane isomers increases dramatically as the number of carbon atoms increases.

Constitutional isomerism is not limited to alkanes—it occurs widely throughout organic chemistry. Constitutional isomers may have different carbon skeletons (as in isobutane and butane), different functional groups (as in ethanol and dimethyl ether), or different locations of a functional group along the chain (as in isopropylamine and propylamine). Regardless of the reason for the isomerism, constitutional isomers are always different compounds with different properties, but with the same formula.

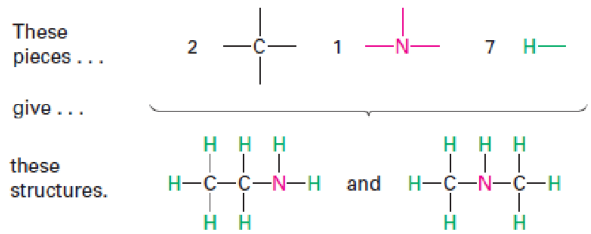


EXAMPLE 3.1 ***Drawing the Structures of Isomers***

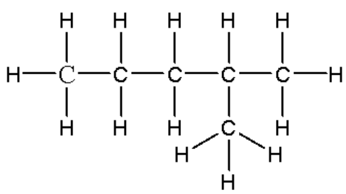
Propose structures for two isomers with the formula C_2H_7N.

Strategy We know that carbon forms four bonds, nitrogen forms three, and hydrogen forms one. Write down the carbon atoms first, and then use a combination of trial and error plus intuition to put the pieces together.

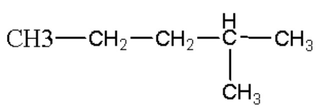
Solution There are two isomeric structures. One has the connection C–C–N, and the other has the connection C–N–C.



Abbreviated Structural Formulas

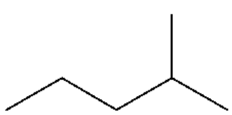


Expand structure

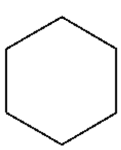


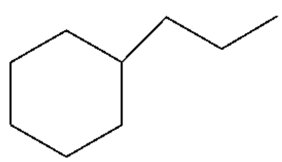
partial Expand structure

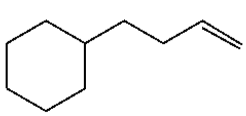
CH3CH2CH2CH(CH3)2 **Condensed structure**

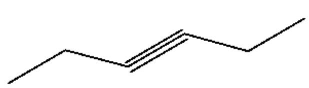


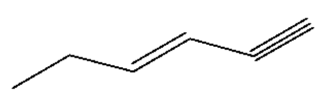
Skeletal structure











1.17 Classification According to Molecular Framework

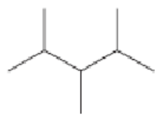
The three main classes of molecular frameworks for organic structures are acyclic, carbocyclic, and heterocyclic compounds.

1.17.a Acyclic Compounds

By **acyclic** (pronounced a′-cyclic), we mean *not cyclic.* Acyclic organic molecules have chains of carbon atoms but no rings. As we have seen, the chains may be unbranched or branched.

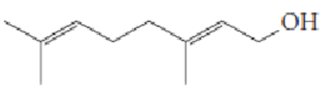
Acyclic compounds contain no rings. **Carbocyclic compounds** contain rings of carbon atoms. **Heterocyclic compounds** have rings containing at least one atom that is *not* carbon.

unbranched chain of eight carbon atoms



branched chain of eight carbon atoms

Pentane is an example of an acyclic compound with an unbranched carbon chain, whereas isopentane and neopentane are also acyclic but have branched carbon frameworks (Sec. 1.9). Figure 1.12 shows the structures of a few acyclic compounds that occur in nature.



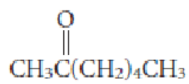
geraniol
(oil of roses)
bp 229–230°C

A branched chain compound used in perfumes

$CH_3(CH_2)_5CH_3$

heptane
(petroleum)
bp 98.4°C

A hydrocarbon present in petroleum, used as a standard in testing the octane rating of gasoline



2-heptanone
(oil of cloves)
bp 151.5°C

A colorless liquid with a fruity odor, in part responsible for the "peppery" odor of blue cheese

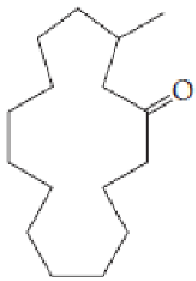
Figure 1.12
Examples of natural acyclic compounds, their sources (in parentheses), and selected characteristics.

Foodcollection/Getty Images

2-Heptanone contributes to the "peppery" odor of blue cheese.

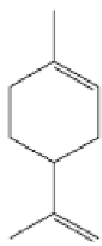
1.17.b Carbocyclic Compounds

Carbocyclic compounds contain rings of carbon atoms. The smallest possible carbocyclic ring has three carbon atoms, but carbon rings come in many sizes and shapes. The rings may have chains of carbon atoms attached to them and may contain multiple bonds. Many compounds with more than one carbocyclic ring are known. Figure 1.13 shows the structures of a few carbocyclic compounds that occur in nature. Five- and six-membered rings are most common, but smaller and larger rings are also found.



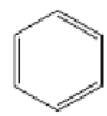
muscone
(musk deer)
bp 327–330°C

A 15-membered ring ketone, used in perfumes



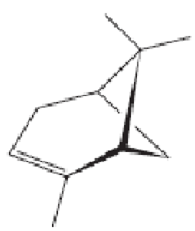
limonene
(citrus fruit oils)
bp 178°C

A ring with two side chains, one of which is branched



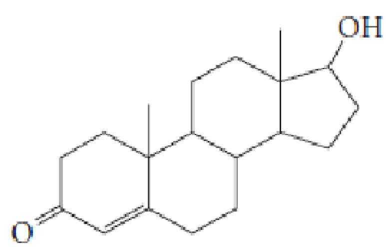
benzene
(petroleum)
mp 5.5°C, bp 80.1°C

A very common ring



α-pinene
(turpentine)
bp 156.2°C

A bicyclic molecule; one would have to break *two* bonds to make it acyclic



testosterone
(testes)
mp 155°C

A male sex hormone in which several rings of common sizes are *fused* together; that is, they share two adjacent carbon atoms

1.17.c Heterocyclic Compounds

Heterocyclic compounds make up the third and largest class of molecular frameworks for organic compounds. In heterocyclic compounds, at least one atom in the ring must be a heteroatom, an atom that is *not* carbon. The most common heteroatoms are oxygen, nitrogen, and sulfur, but heterocyclics with other elements are also known. More than one heteroatom may be present and, if so, the heteroatoms may be alike or different. Heterocyclic rings come in many sizes, may contain multiple bonds, may have carbon chains or rings attached to them, and in short may exhibit a great variety of structures. Figure 1.14 shows the structures of a few natural products that contain heterocyclic rings. In these abbreviated structural formulas, the symbols for the heteroatoms are shown, but the carbons are indicated using lines only.

The structures in Figures 1.12 through 1.14 show not only the molecular frameworks, but also various groups of atoms that may be part of or attached to the frameworks. Fortunately, these groups can also be classified in a way that helps simplify the study of organic chemistry.

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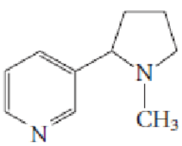
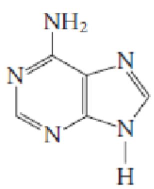
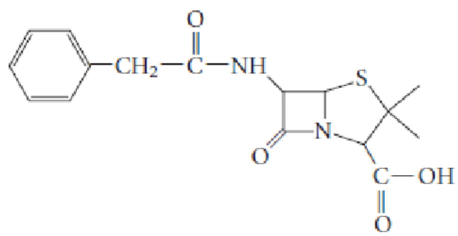
Clover, a source of coumarin.



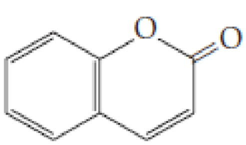
nicotine
bp 246°C



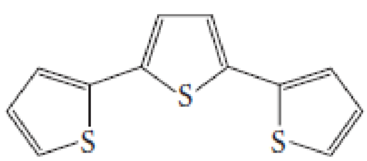
adenine
mp 360–365°C
(decomposes)



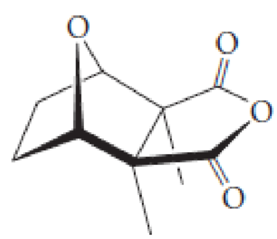
penicillin-G
(amorphous solid)



coumarin
mp 71°C



α-terthienyl
mp 92–93°C

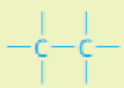
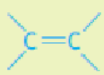
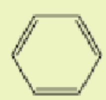
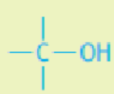
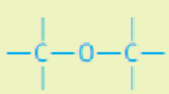


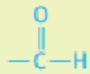
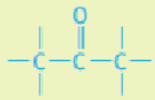
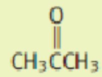
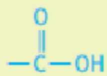
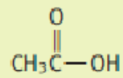
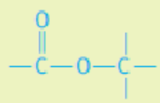
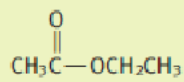
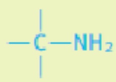
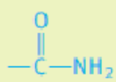
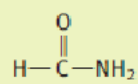
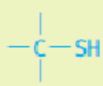
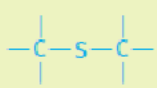
cantharidin
mp 218°C

1.18 Classification According to Functional Group

Certain groups of atoms have chemical properties that depend only moderately on the molecular framework to which they are attached. These groups of atoms are called **functional groups**. The hydroxyl group, —OH, is an example of a functional group, and compounds with this group attached to a carbon framework are called alcohols. In most organic reactions, some chemical change occurs at the functional group, but the rest of the molecule keeps its original structure. This maintenance of most of the structural formula throughout a chemical reaction greatly simplifies our study of organic chemistry. It allows us to focus attention on the chemistry of the various functional groups. We can study classes of compounds instead of having to learn the chemistry of each individual compound.

Table 1.6 The Main Functional Groups

	Structure	Class of compound	Specific example	Common name of the specific example
A. Functional groups that are a part of the molecular framework		alkane	$CH_3—CH_3$	ethane, a component of natural gas
		alkene	$CH_2=CH_2$	ethylene, used to make polyethylene
	$—C\equiv C—$	alkyne	$HC\equiv CH$	acetylene, used in welding
		arene		benzene, raw material for polystyrene and phenol
B. Functional groups containing oxygen				
1. With carbon–oxygen single bonds		alcohol	CH_3CH_2OH	ethyl alcohol, found in beer, wines, and liquors
		ether	$CH_3CH_2OCH_2CH_3$	diethyl ether, once a common anesthetic

*2. With carbon–oxygen double bonds**		aldehyde	$CH_2{=}O$	formaldehyde, used to preserve biological specimens
		ketone		acetone, a solvent for varnish and rubber cement
3. With single and double carbon–oxygen bonds		carboxylic acid		acetic acid, a component of vinegar
		ester		ethyl acetate, a solvent for nail polish and model airplane glue
*C. Functional groups containing nitrogen***		primary amine	$CH_3CH_2NH_2$	ethylamine, smells like ammonia
	$-C\equiv N$	nitrile	$CH_2{=}CH{-}C\equiv N$	acrylonitrile, raw material for making Orlon
D. Functional group with oxygen and nitrogen		primary amide		formamide, a softener for paper
E. Functional group with halogen	$-X$	alkyl or aryl halide	CH_3Cl	methyl chloride, refrigerant and local anesthetic
F. Functional groups containing sulfur[†]		thiol (also called mercaptan)	CH_3SH	methanethiol, has the odor of rotten cabbage
		thioether (also called sulfide)	$(CH_2{=}CHCH_2)_2S$	diallyl sulfide, has the odor of garlic