General Chemistry
WS 2022/23

Dr. Lars Birlenbach
Physikalische Chemie 1 (PC1)
AR-F 0102
Tel.: 0271 740 2817
eMail: birlenbach@chemie.uni-siegen.de

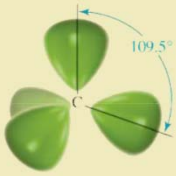
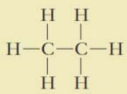
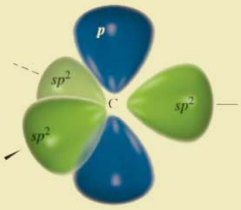
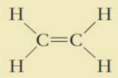
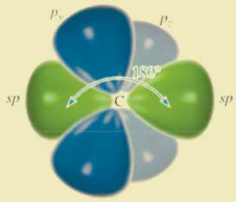
- Website (Slides, Exercises):
- http://www.chemie.uni-siegen.de/pc/lehre/genchem/

Login Data for slides:
User: Ludwig
Passwort: Boltzmann

Organic Chemistry

- **Organic chemistry** deals with carbon-containing compounds that contain C-C or C-H bonds, and sometimes a few other elements such as oxygen, nitrogen, sulfur, phosphorus, and the halogens.
  - there are many more compounds that contain carbon than there are compounds that do not
  - the molecules containing carbon can be very simple and very complex
    - methane molecule contains five atoms per molecule
    - DNA contains tens of billions of atoms per molecule.

Why is that?

Hybridization and Resulting Geometry	Orbitals Used by Each C Atom		Bonds Formed by Each C Atom	Example
sp^3, tetrahedral	four sp^3 hybrids		four σ bonds	ethane 
sp^2, trigonal planar	three sp^2 hybrids, one p orbital		three σ bonds, one π bond	ethylene 
sp, linear	two sp hybrids, two p orbitals		two σ bonds, two π bonds	acetylene H—C≡C—H

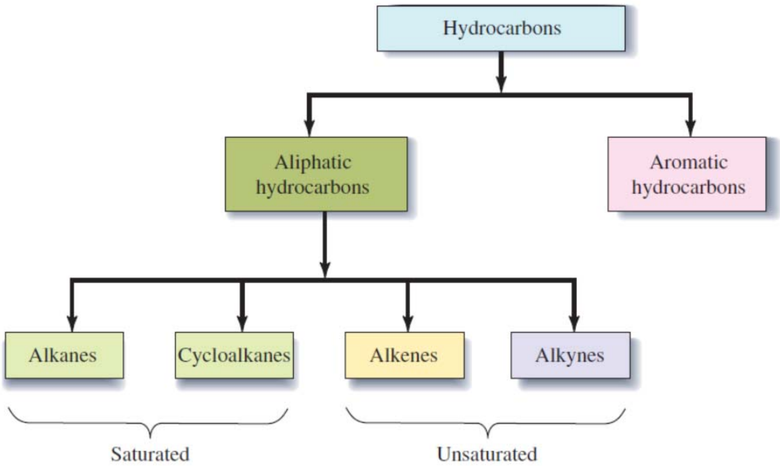


Figure 27-1 Classification of hydrocarbons.

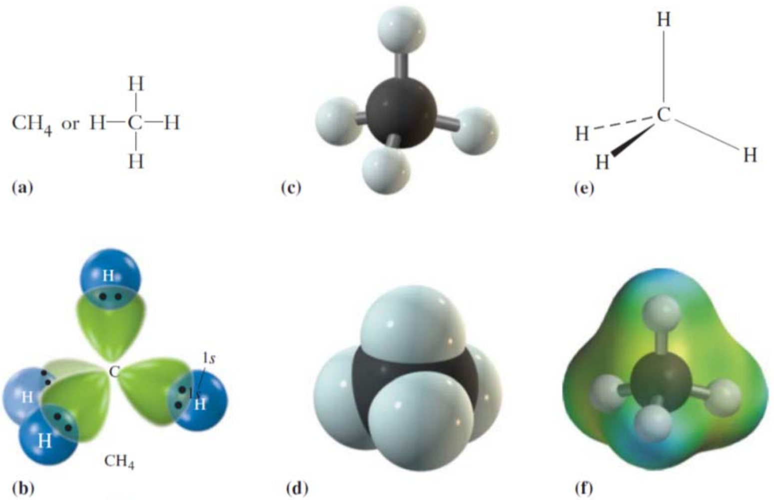
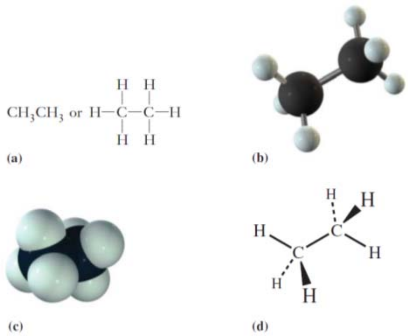


Figure 27-2 Representations of a molecule of methane, CH_4. (a) The condensed and Lewis formulas for methane. (b) The overlap of the four sp^3 carbon orbitals with the *s* orbitals of four hydrogen atoms forms a tetrahedral molecule. (c) A ball-and-stick model, (d) a space-filling model, (e) a three-dimensional representation that uses the wedged line to indicate a bond coming forward and a dashed line to represent a bond projecting backward, and (f) an ECP plot.

Alkanes



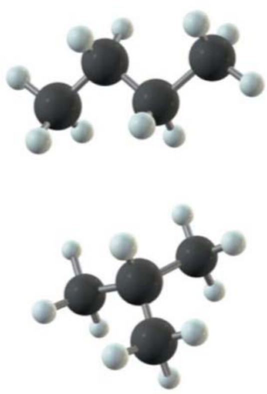


Figure 27-4 Ball-and-stick and space-filling models and a three-dimensional representation of propane, C_3H_8.

Figure 27-5 Ball-and-stick models of the two isomeric C_4H_{10} hydrocarbons, butane, $CH_3CH_2CH_2CH_3$, and methylpropane, CH_3CHCH_3 (with CH_3 on the central carbon).

Homologous series

Molecular Formula	IUPAC Name	Normal bp (°C)	
CH_4	methane	−161	
C_2H_6	ethane	−88	
C_3H_8	propane	−42	
C_4H_{10}	butane	+0.6	
C_5H_{12}	pentane	36	
C_6H_{14}	hexane	69	
C_7H_{16}	heptane	98	
C_8H_{18}	octane	126	
C_9H_{20}	nonane	150	
$C_{10}H_{22}$	decane	174	
$C_{11}H_{24}$	undecane	194.5	
$C_{12}H_{26}$	dodecane	214.5	
$C_{13}H_{28}$	tridecane	234	
$C_{14}H_{30}$	tetradecane	252.5	
$C_{15}H_{32}$	pentadecane	270.5	
$C_{16}H_{34}$	hexadecane	287.5	
$C_{17}H_{36}$	heptadecane	303	
$C_{18}H_{38}$	octadecane	317	
$C_{19}H_{40}$	nonadecane	330	
$C_{20}H_{42}$	eicosane	205 (at 15 torr)	36.7

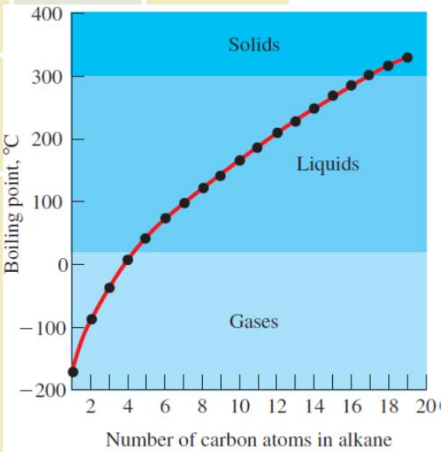


Figure 27-6 A plot of normal boiling point versus the number of carbon atoms in straight-chain, saturated hydrocarbons.

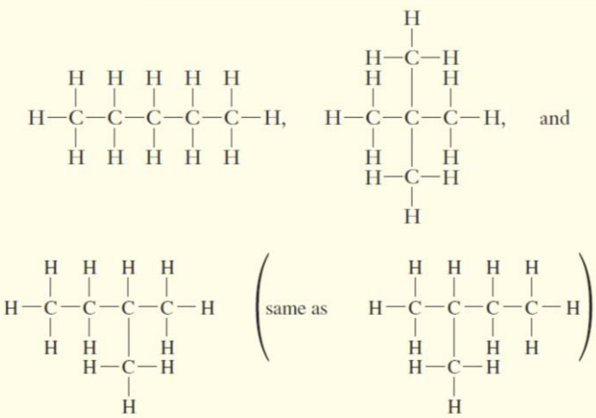
Example 27-1 Isomeric Alkanes

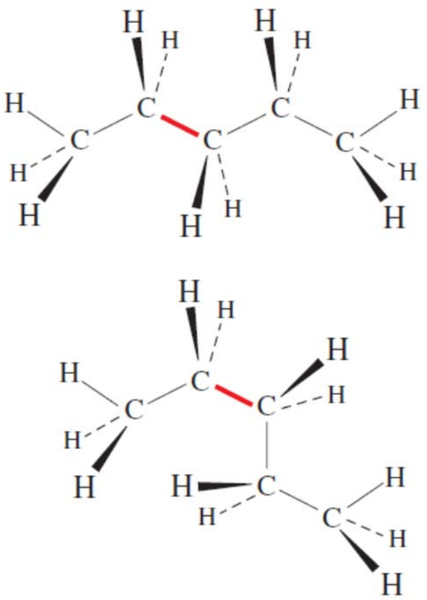
MOLECULAR REASONING

Write the Lewis formula of each of the three isomers having the molecular formula of C_5H_{12}. The boiling points of the three isomers are 9.5°C, 27.9°C, and 36.1°C. Match each compound with its boiling point.

Solution

The three compounds are $CH_3C(CH_3)_3$, bp = 9.5°C; $CH_3CH_2CH(CH_3)_2$, bp = 27.9°C; and $CH_3CH_2CH_2CH_2CH_3$, bp = 36.1°C.





Rotation about a single bond does *not* generate a different isomer. For example, the following two drawings differ only by rotation about the bond shown in red; they both represent the same isomer of C_5H_{12} (see Example 27-1).

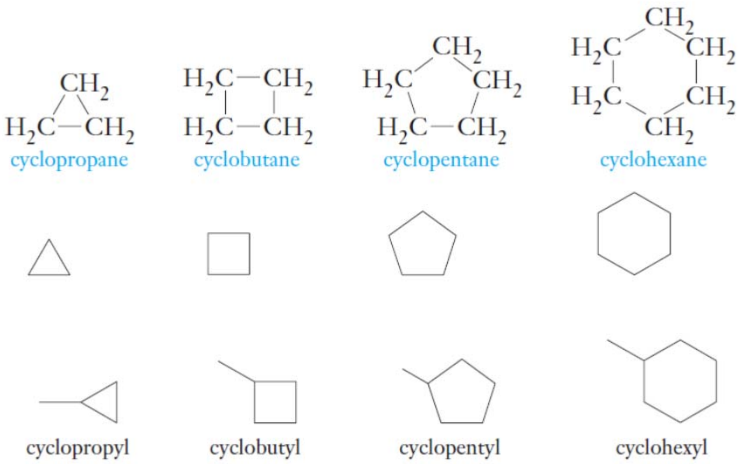
Table 27-3 Isomeric C_6H_{14} Alkanes

IUPAC Name	Formula
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
2-methylpentane	$CH_3CH_2CH_2CH(CH_3)CH_3$
3-methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$
2,2-dimethylbutane	$CH_3CH_2C(CH_3)_2CH_3$
2,3-dimethylbutane	$CH_3CH(CH_3)—CH(CH_3)CH_3$

Table 27-4 Numbers of Possible Constitutional Isomers of Alkanes

Formula	Isomers
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{11}H_{24}$	159
$C_{12}H_{26}$	355
$C_{13}H_{28}$	802
$C_{14}H_{30}$	1,858
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{25}H_{52}$	36,797,588
$C_{30}H_{62}$	4,111,846,763

Cycloalkanes



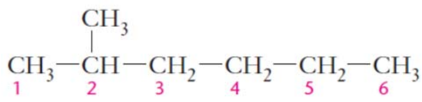
Lars Birlenbach birlenbach@chemie.uni-siegen.de

Naming Saturated Hydrocarbons

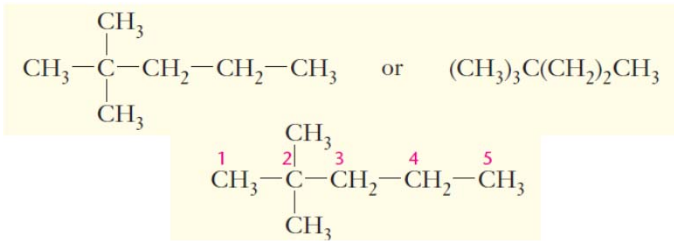
SUMMARY OF IUPAC RULES FOR NAMING ALKANES

1. Find the longest chain of C atoms. Choose the base name that describes the number of C atoms in this chain, with the ending *-ane* (Table 27-2). The longest chain may not be obvious at first if branches of different sizes are present.
2. Number the C atoms in this longest chain beginning at the end nearest the first branching. If necessary, go to the second branch closest to an end, and so on, until a difference is located. If there is branching at equal distances from both ends of the longest chain, begin numbering at the end nearest the branch that is first in alphabetical order.
3. Assign the name and position number to each substituent. Arrange the substituents in alphabetical order. Hyphenated prefixes, such as *tert-* and *sec-*, are not used in alphabetization of the substituents.
4. Use the appropriate prefix to group like substituents: *di-* = 2, *tri-* = 3, *tetra-* = 4, *penta-* = 5, and so on. Don't consider these prefixes when alphabetizing attached groups.
5. Write the name as a single word. Use hyphens to separate numbers and letters (plus some hyphenated prefixes) and commas to separate numbers. Don't leave any spaces.

Lars Birlenbach birlenbach@chemie.uni-siegen.de

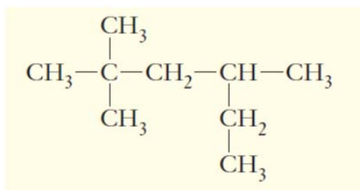


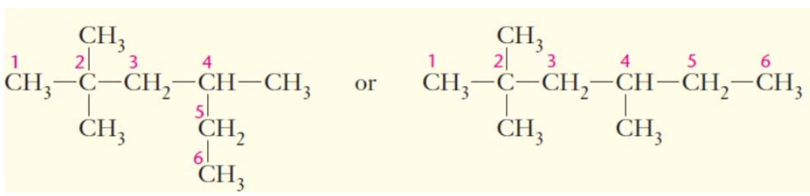
2-methylhexane



2,2-dimethylpentane

Lars Birlenbach birlenbach@chemie.uni-siegen.de 13



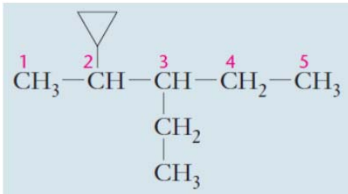


2,2,4-trimethylhexane

Lars Birlenbach birlenbach@chemie.uni-siegen.de 14

Writing Formulas from Names

Write the structure for the compound 2-cyclopropyl-3-ethylpentane



Unsaturated Hydrocarbons: Alkenes

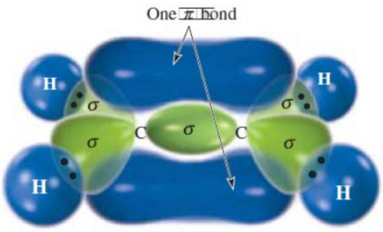
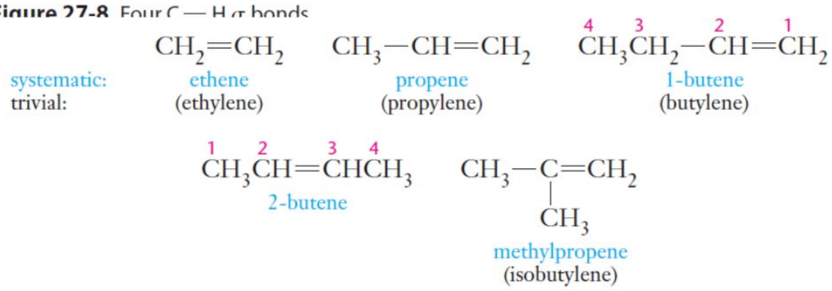
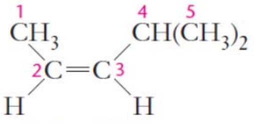
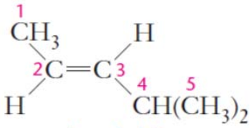


Figure 27-8 Four C — H σ bonds





cis-4-methyl-2-pentene



trans-4-methyl-2-pentene

1 2 3 4
$CH_2=CH-CH=CH_2$

1,3-butadiene

4 3 2 1
$CH_3-CH=C=CH_2$

1,2-butadiene

Unsaturated Hydrocarbons: Alkynes

$CH\equiv CH$

ethyne
(acetylene)

$CH_3-C\equiv CH$

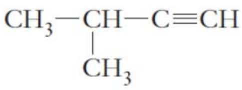
propyne

$CH_3-CH_2-C\equiv CH$

1-butyne

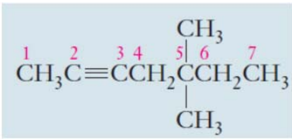
$CH_3-C\equiv C-CH_3$

2-butyne

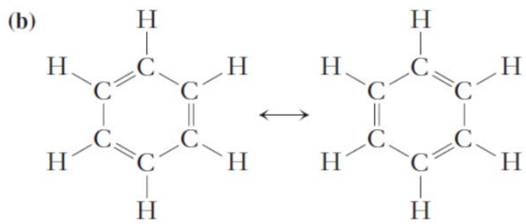


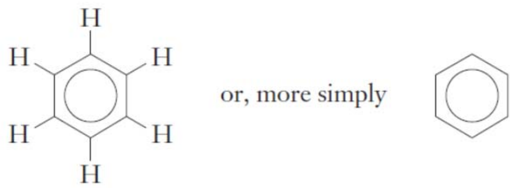
3-methyl-1-butyne

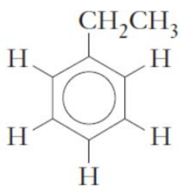
Write the structural formula of 5,5-dimethyl-2-heptyne

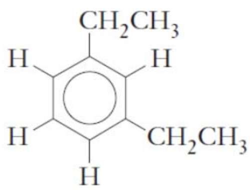


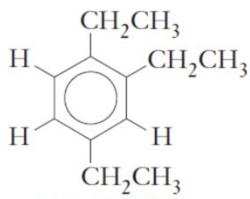
Aromatic Hydrocarbons

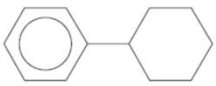


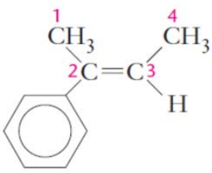



ethylbenzene

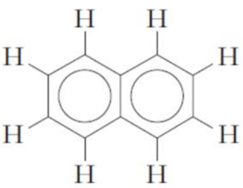

m-diethylbenzene, or 1,3-diethylbenzene


1,2,4-triethylbenzene

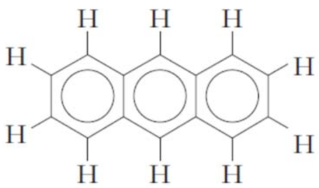

phenylcyclohexane


cis-2-phenyl-2-butene

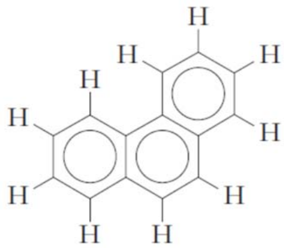
Condensed aromatic systems



naphthalene, $C_{10}H_8$

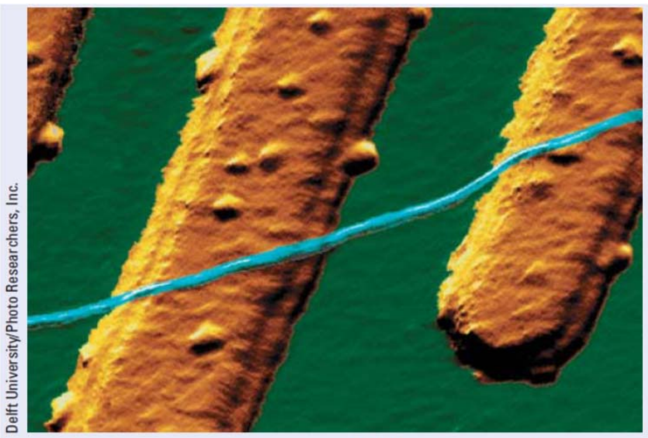


anthracene, $C_{14}H_{10}$



phenanthrene, $C_{14}H_{10}$

Carbon nanotubes



A colored atomic force microscope (AFM) image of a carbon nanotube wire (blue) on platinum electrodes (yellow). The nanotube is 1.5 nm across, a mere 10 atoms wide. This is

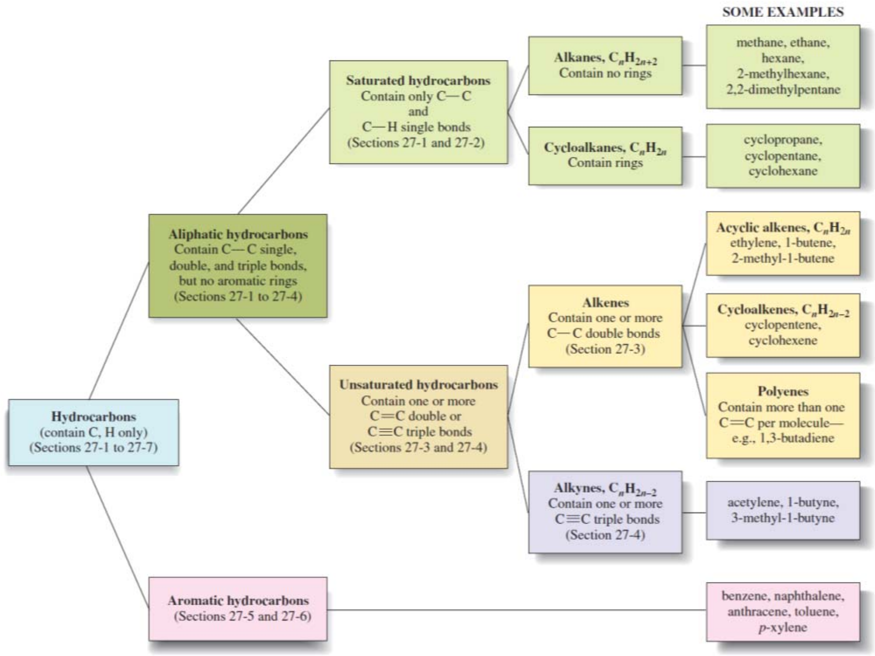
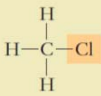
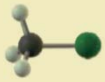
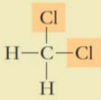
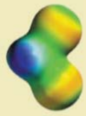
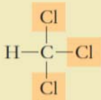
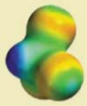
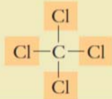
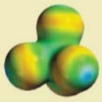


Figure 27-13 A classification of hydrocarbons.

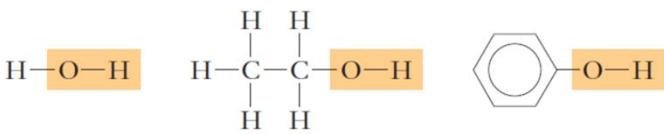
Functional Groups

- Organic Halides
- Alcohols and Phenols
- Ethers
- Aldehydes and Ketones
- Amines
- Carboxylic Acids
- Some Derivatives of Carboxylic Acids

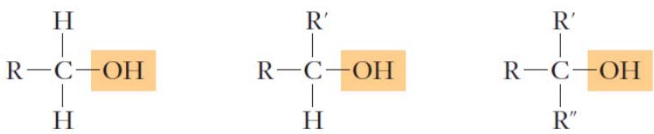
Table 27-7 Some Organic Halides

Formula	Structural Formula	Ball-and-Stick Model	Electrostatic Charge Potential Plot	bp (°C)	IUPAC Name / Common Name
CH_3Cl				−23.8	chloromethane / methyl chloride
CH_2Cl_2				40.2	dichloromethane / methylene chloride
$CHCl_3$				61	trichloromethane / chloroform
CCl_4				76.8	tetrachloromethane / carbon tetrachloride

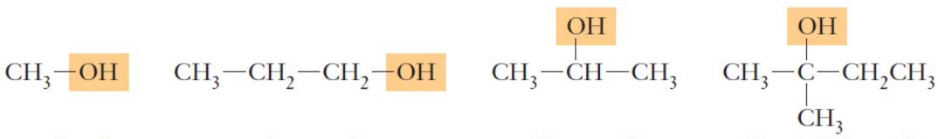
Alcohols and Phenoles



water ethanol phenol



a primary (1°) alcohol a secondary (2°) alcohol a tertiary (3°) alcohol



methanol
methyl alcohol
(wood alcohol)

1-propanol
propyl alcohol
(a primary alcohol)

2-propanol
isopropyl alcohol
(a secondary alcohol)

2-methyl-2-butanol
t-pentyl alcohol
(a tertiary alcohol)

Physical Properties

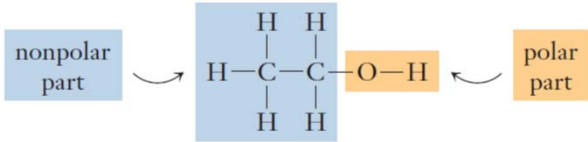
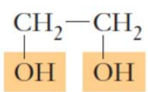


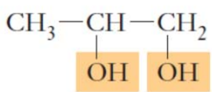
Table 27-8

Name	Formula	Normal bp (°C)	Solubility in H_2O (g/100 g at 20°C)
methanol	CH_3OH	65	miscible
ethanol	CH_3CH_2OH	78.5	miscible
1-propanol	$CH_3CH_2CH_2OH$	97	miscible
1-butanol	$CH_3CH_2CH_2CH_2OH$	117.7	7.9
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	137.9	2.7
1-hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	155.8	0.59

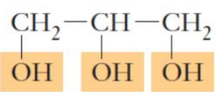
polyols are alcohols that contain more than one -OH group per molecule



1,2-ethanediol
ethylene glycol
(the major ingredient in permanent antifreeze)

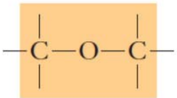


1,2-propanediol
propylene glycol



1,2,3-propanetriol
glycerine or glycerol
(a moisturizer in cosmetics)

Ethers



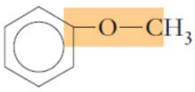
H—O—H
water

R—O—H
alcohol

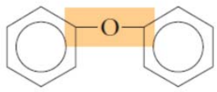
R—O—R′
ether

$H_3C—O—CH_3$
methoxymethane
dimethyl ether
(an aliphatic ether)

$H_3C—O—CH_2CH_3$
methoxyethane
methyl ethyl ether
(an aliphatic ether)



methoxybenzene
methyl phenyl ether
anisole
(a mixed ether)

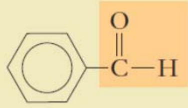


phenoxybenzene
diphenyl ether
(an aromatic ether)

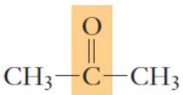
Functional Groups

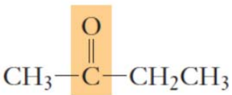
- Organic Halides
- Alcohols and Phenols
- Ethers
- Aldehydes and Ketones
- Amines
- Carboxylic Acids
- Some Derivatives of Carboxylic Acids

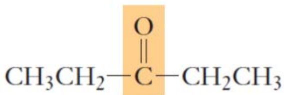
Aldehydes

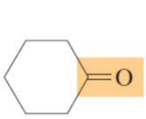
Common Name	Formula
formaldehyde (methanal)	$H-\overset{\overset{\displaystyle O}{\|}}{C}-H$
acetaldehyde (ethanal)	$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$
propionaldehyde (propanal)	$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}-H$
benzaldehyde	

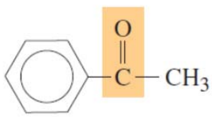
Ketones

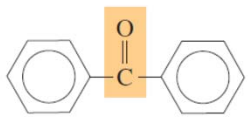

acetone

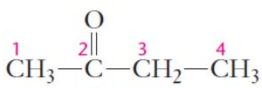

methyl ethyl ketone

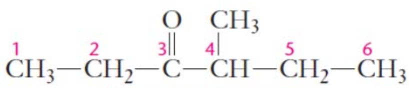

diethyl ketone


cyclohexanone

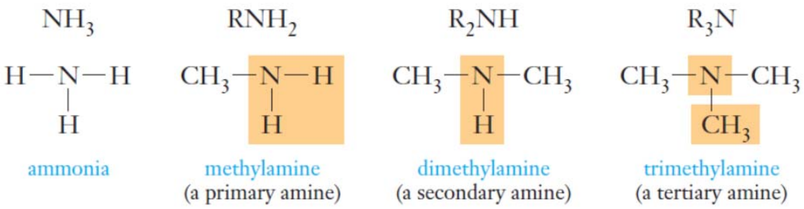

acetophenone
(methyl phenyl ketone)

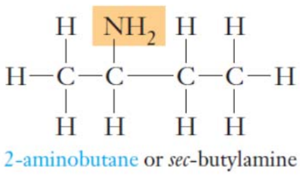

benzophenone
(diphenyl ketone)

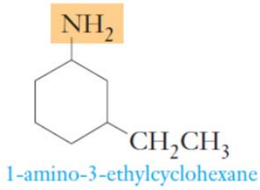

butanone


4-methyl-3-hexanone

Amines



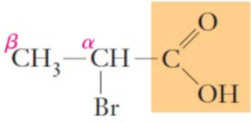




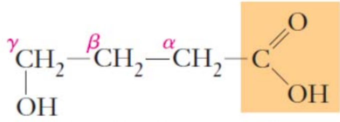
Carboxylic Acids

Table 27-11 Some Aliphatic Carboxylic Acids

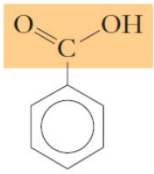
Formula	Common Name	IUPAC Name
$HCOOH$	formic acid	methanoic acid
CH_3COOH	acetic acid	ethanoic acid
CH_3CH_2COOH	propionic acid	propanoic acid
$CH_3CH_2CH_2COOH$	butyric acid	butanoic acid
$CH_3CH_2CH_2CH_2CH_2COOH$	caproic acid	hexanoic acid
$CH_3(CH_2)_{10}COOH$	lauric acid	dodecanoic acid
$CH_3(CH_2)_{14}COOH$	palmitic acid	hexadecanoic acid
$CH_3(CH_2)_{16}COOH$	stearic acid	octadecanoic acid



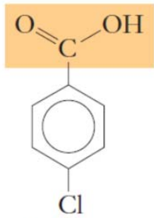
2-bromopropanoic acid
(α-bromopropionic acid)



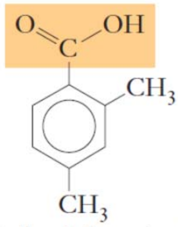
4-hydroxybutanoic acid
(γ-hydroxybutyric acid)



benzoic acid

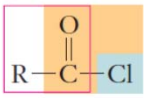


p-chlorobenzoic acid

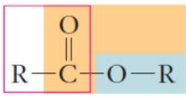


2,4-dimethylbenzoic acid

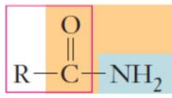
Some Derivatives of Carboxylic Acids



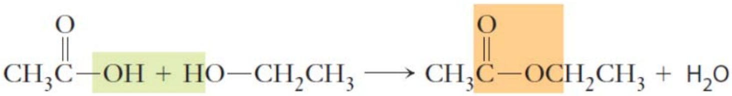
an acyl chloride
(an acid chloride)



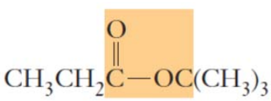
an ester



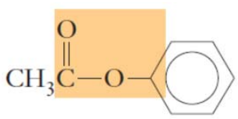
an amide



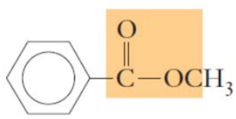
acetic acid ethyl alcohol ethyl acetate



t-butyl propionate



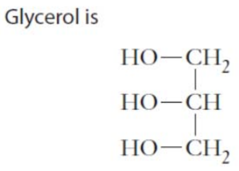
phenyl acetate

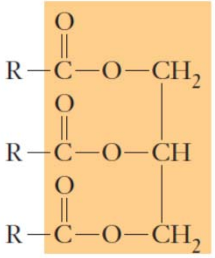


methyl benzoate

Fats (solids) and oils (liquids)

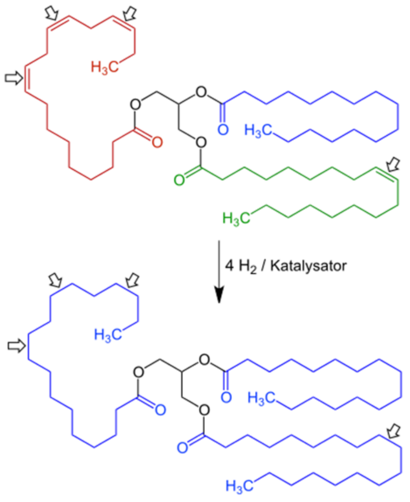
- are esters of glycerol and aliphatic acids of high molecular weight
- **Fatty acids** are long-chain organic acids whose esters occur in fats and oils.





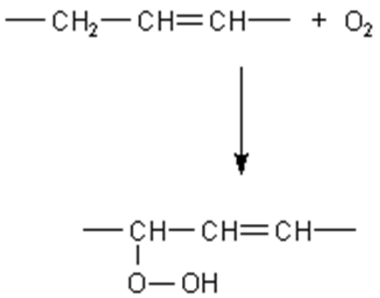
- **Waxes** are esters of fatty acids and alcohols other than glycerol

Hydrogenation of fats

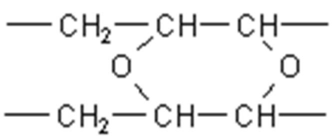


Bildquelle: Wikipedia

Autoxidation



Linoleic acid is used in making quick-drying oils, which are useful in oil paints and varnishes. These applications exploit the easy reaction of the linoleic acid with oxygen in air, which leads to crosslinking and formation of a stable film called linoxyn



Bildquelle: chemieunterricht.de

Carbohydrates

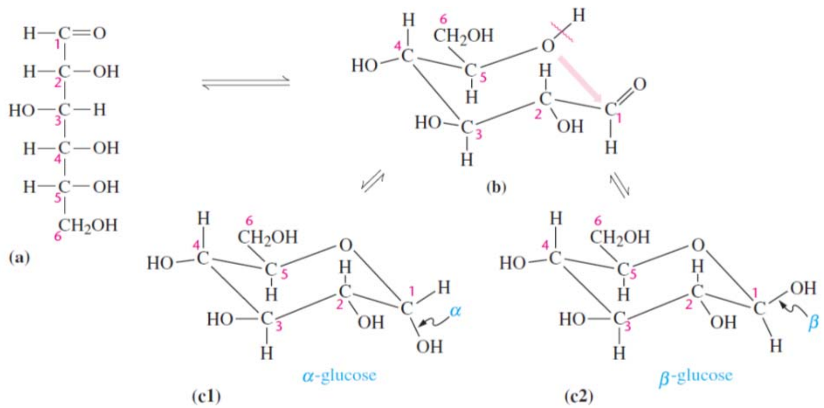
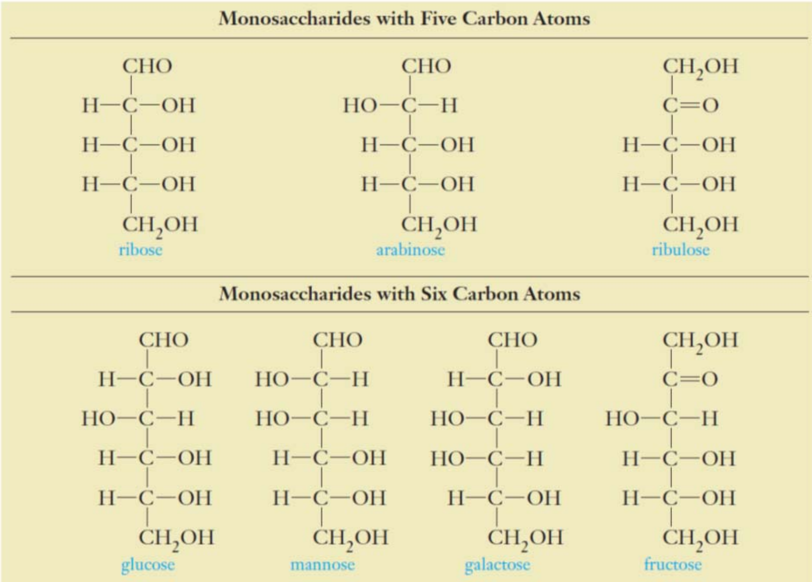


Table 28-4 Some Important Monosaccharides



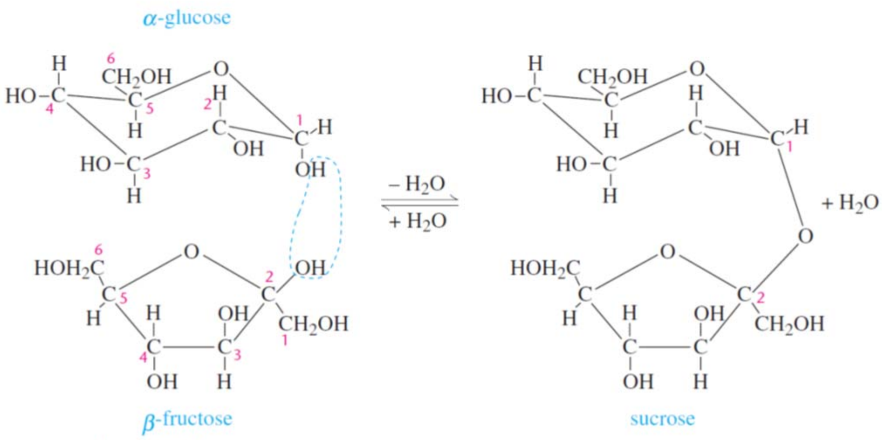
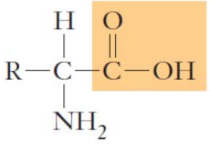


Figure 28-11 Formation of sucrose by the condensation of an α-glucose molecule with a β-fructose molecule.

Figure 28-13 A small portion of amylopectin, or glycogen (a biopolymer).

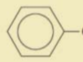
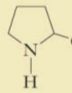
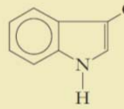
Amino Acids

a-Amino acids are substituted carboxylic acids with the general structure



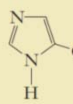
where R can be either an alkyl or an aryl group. a-Amino acids are the components of proteins, which make up the muscle and tissue of animals

Common Amino Acids Found in Proteins

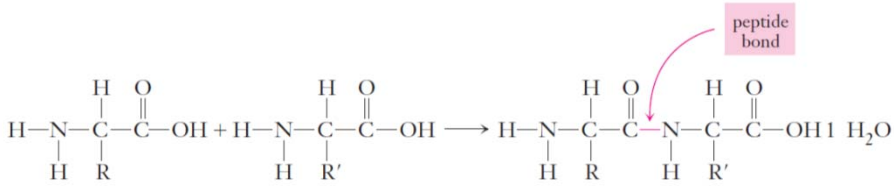
Nonpolar R Groups			
alanine (Ala)	$CH_3CHCOOH$ NH_2	phenylalanine (Phe)	 $CH_2CHCOOH$ NH_2
glycine (Gly)	$HCHCOOH$ NH_2	proline (Pro)	 $COOH$
isoleucine (Ile)	CH_3 $CH_3CH_2CHCHCOOH$ NH_2	tryptophan (Trp)	 $CH_2CHCOOH$ NH_2
leucine (Leu)	$(CH_3)_2CHCH_2CHCOOH$ NH_2		
methionine (Met)	$CH_3SCH_2CH_2CHCOOH$ NH_2	valine (Val)	$(CH_3)_2CHCHCOOH$ NH_2

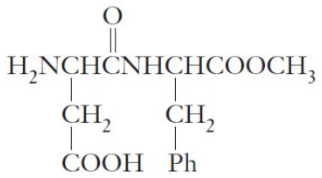
A **protein** is a biopolymer, of molecular weight typically 5000 g/mol or greater, consisting of one or more polypeptide chains. The a-amino acids that occur in nearly all proteins are the L optical isomer.

Polar, Neutral R Groups			
asparagine (Asn)	O ‖ $H_2NCCH_2CHCOOH$ NH_2	serine (Ser)	$HOCH_2CHCOOH$ NH_2
glutamine (Gln)	O ‖ $H_2NCCH_2CH_2CHCOOH$ NH_2	threonine (Thr)	OH $CH_3CHCHCOOH$ NH_2

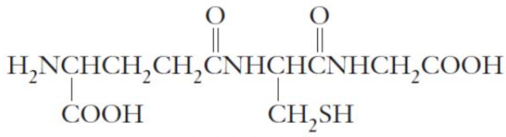
Polar, Acidic R Groups		Polar, Basic R Groups	
aspartic acid (Asp)	$HOOCCH_2CHCOOH$ NH_2	arginine (Arg)	NH ‖ $H_2NCNHCH_2CH_2CH_2CHCOOH$ NH_2
glutamic acid (Glu)	$HOOCCH_2CH_2CHCOOH$ NH_2		
cysteine (Cys)	$HSCH_2CHCOOH$ NH_2	histidine (His)	 $CH_2CHCOOH$ NH_2
tyrosine (Tyr)	HO  $CH_2CHCOOH$ NH_2	lysine (Lys)	$H_2NCH_2CH_2CH_2CH_2CHCOOH$ NH_2

Polypeptides and Proteins





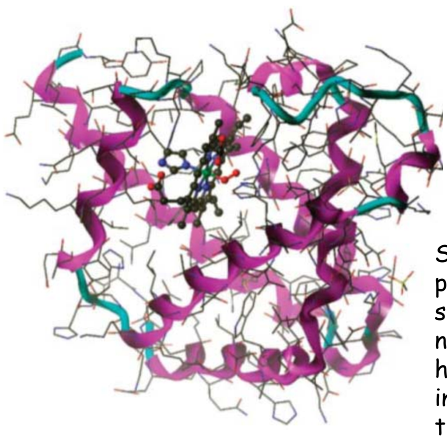
aspartame
(Asp-Phe-OCH_3)



glutathione
(Gln-Cys-Gly)

Each protein consists of one or more polypeptide chains with a unique sequence of amino acids. The order of these monomers is termed the **primary structure** of the protein.

Val-Leu-Ser-Glu-Gly-Glu-Trp-Gln-Leu-Val-Leu-His-Val-Trp-Ala-Lys-Val-
Glu-Ala-Asp-Val-Ala-Gly-His-Gly-Gln-Asp-Ile-Leu-Ile-Arg-Leu-Phe-Lys-
Ser-His-Pro-Glu-Thr-Leu-Glu-Lys-Phe-Asp-Arg-Phe-Lys-His-Leu-Lys-
Thr-Glu-Ala-Glu-Met-Lys-Ala-Ser-Glu-Asp-Leu-Lys-Lys-His-Gly-Val-Thr-
Val-Leu-Thr-Ala-Leu-Gly-Ala-Ile-Leu-Lys-Lys-Lys-Gly-His-His-Glu-Ala-
Glu-Leu-Lys-Pro-Leu-Ala-Gln-Ser-His-Ala-Thr-Lys-His-Lys-Ile-Pro-Ile-Lys-
Tyr-Leu-Glu-Phe-Ile-Ser-Glu-Ala-Ile-Ile-His-Val-Leu-His-Ser-Arg-His-
Pro-Gly-Asn-Phe-Gly-Ala-Asp-Ala-Gln-Gly-Ala-Met-Asn-Lys-Ala-Leu-
Glu-Leu-Phe-Arg-Lys-Asp-Ile-Ala-Ala-Lys-Tyr-Lys-Glu-Leu-Gly-Tyr-Gln-Gly



The **secondary structure** of a protein is the arrangement in space of the polypeptide backbone, without reference to the conformations of the side chains (R groups).

The *tertiary structure* of a protein describes the overall shape of the protein, including the side chains and any other nonpeptide components of the protein.

Some proteins consist of multiple polypeptide units called *subunits*. These subunits are held to one another by noncovalent interactions such as hydrogen bonding, dipole–dipole interactions, or ionic attractions to form the *quaternary structure* of the protein.

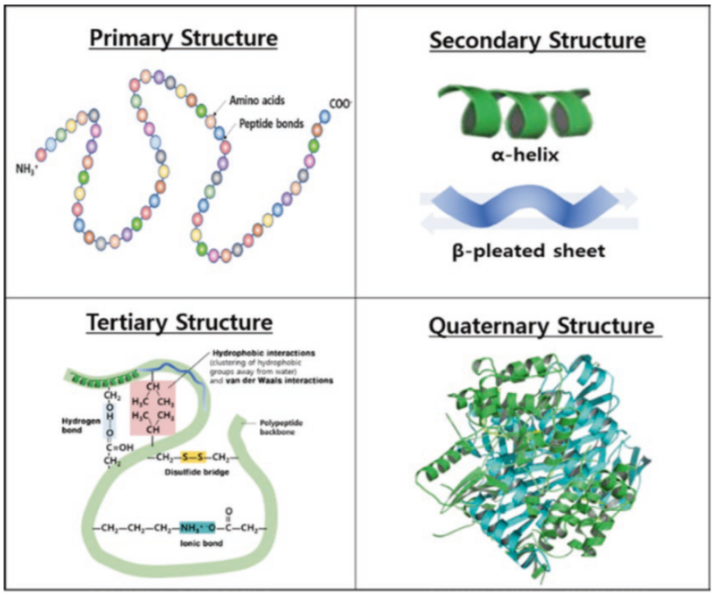
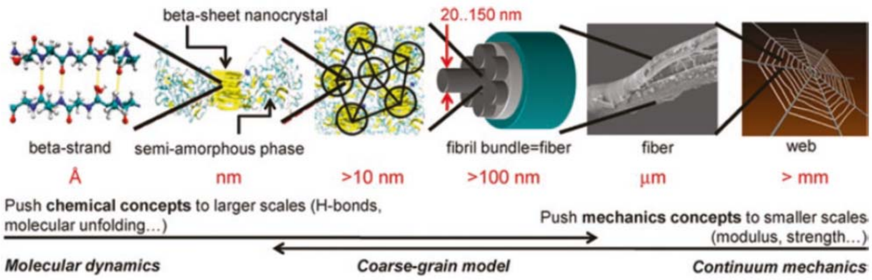


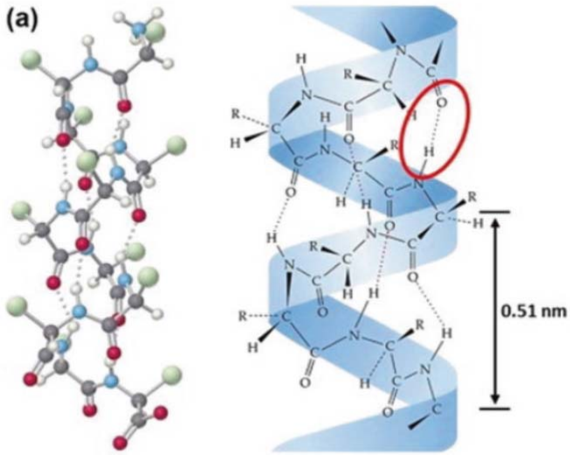
Fig. 10.2 Levels of protein organization

Spider Silk

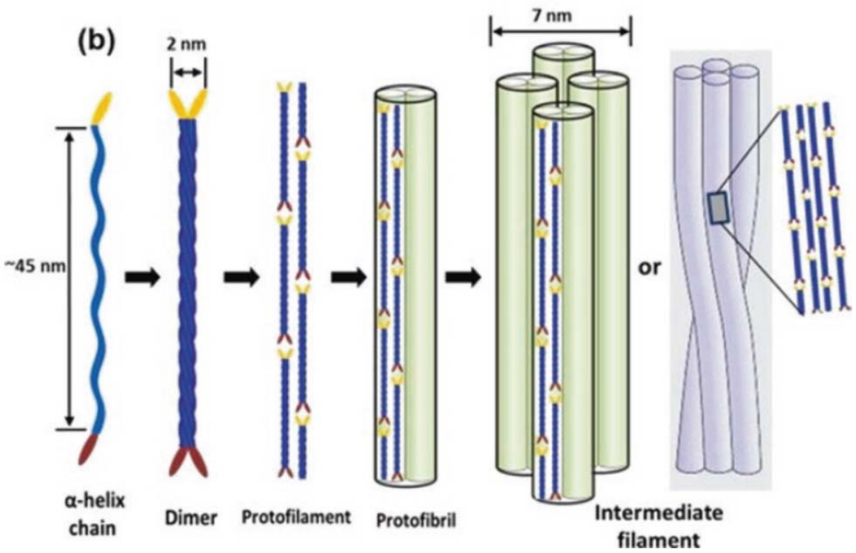


Schematic representation of the hierarchical structure of spider silk including detailed views of the microscale structure and flaws in silk fibers.

Keratin based biomaterials



ball-and-stick model of the polypeptide chain, and α-helix showing the location of the hydrogen bonds (red ellipse) and the 0.51 nm pitch of the helix

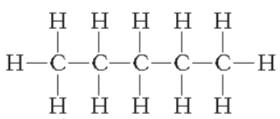


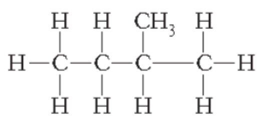
Schematic drawing of the intermediate filament formation: α-helix chains twist to form the dimers, which assemble to form the proto-filament. Four proto-filaments organize into the intermediate filament

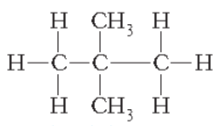
Isomerism

- Isomers
  - Constitutional (structural)
  - Stereoisomers
    - Geometric (*cis-* or *trans-*)
    - Optical (enantiomers) (D- or L-)

Constitutional Isomers


pentane, C_5H_{12}

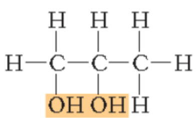

methylbutane
isopentane, C_5H_{12}

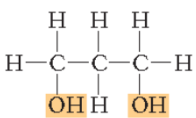

dimethylpropane
neopentane, C_5H_{12}

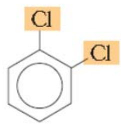
$CH_2{=}CHCH{=}CHCH_2CH_3$
1,3-hexadiene, C_6H_{10}

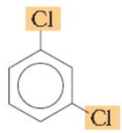
$CH_2{=}CHCH_2CH{=}CHCH_3$
1,4-hexadiene, C_6H_{10}

$CH_2{=}CHCH_2CH_2CH{=}CH_2$
1,5-hexadiene, C_6H_{10}

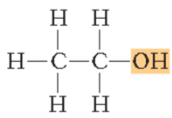

1,2-propanediol, $C_3H_8O_2$

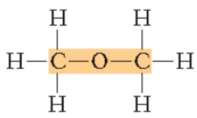

1,3-propanediol, $C_3H_8O_2$

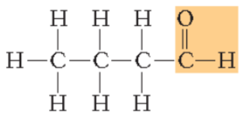

o-dichlorobenzene, $C_6H_4Cl_2$

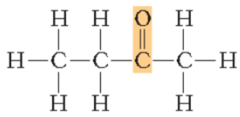

m-dichlorobenzene, $C_6H_4Cl_2$


p-dichlorobenzene, $C_6H_4Cl_2$


ethanol, C_2H_6O


methoxymethane, C_2H_6O
(dimethyl ether)


butanal, C_4H_8O
(butyraldehyde)


butanone, C_4H_8O
(methyl ethyl ketone)

Stereoisomers

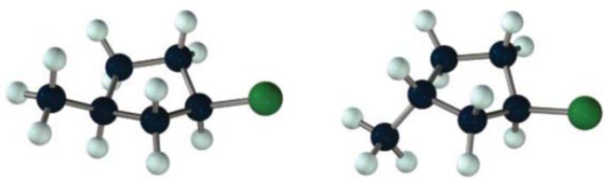

(a) (b)

Figure 28-2 Models of (a) *cis*-1-chloro-3-methylcyclopentane and (b) *trans*-1-chloro-3-methylcyclopentane.

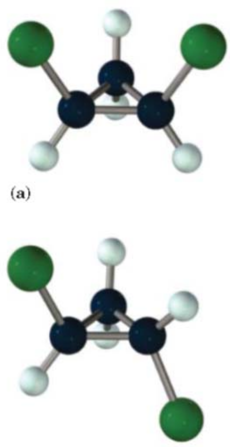
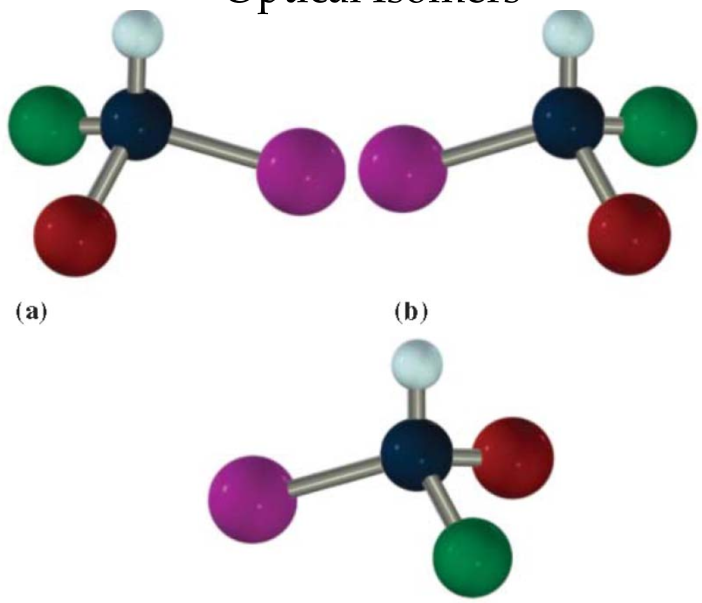

(a)
(b)

Figure 28-1 Models of (a) *cis*-dichlorocyclopropane and (b) *trans*-dichlorocyclopropane.

Optical Isomers



No Optical Isomers

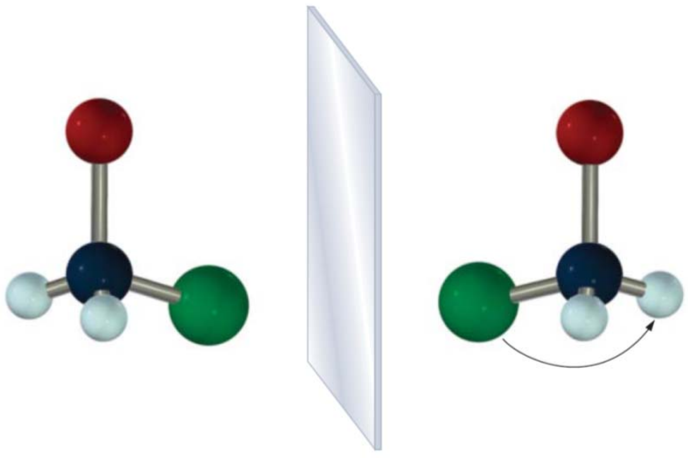
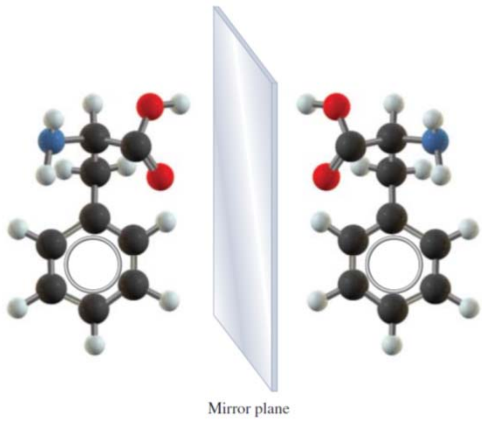


Figure 28-4 Models of two mirror-image forms of bromochloromethane, CH_2BrCl. The two models are the same (superimposable), so they are achiral. CH_2BrCl does *not* exhibit optical isomerism.

Optical Isomers

Ball-and-stick model of L-phenylalanine.



Conformations

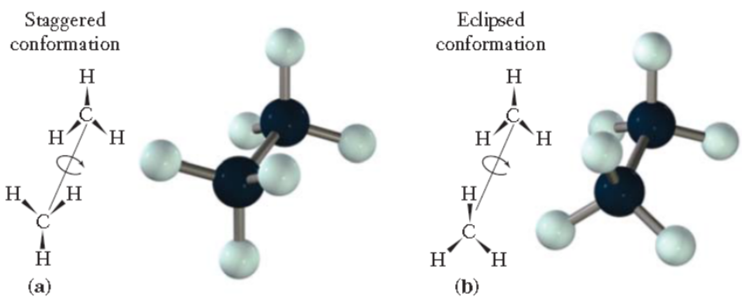


Figure 28-7 Two possible conformations of ethane. (a) Staggered. (b) Eclipsed. Rotation of one CH_3 group about the C — C single bond, as shown by the curved arrows, converts one conformation to the other.

Conformations

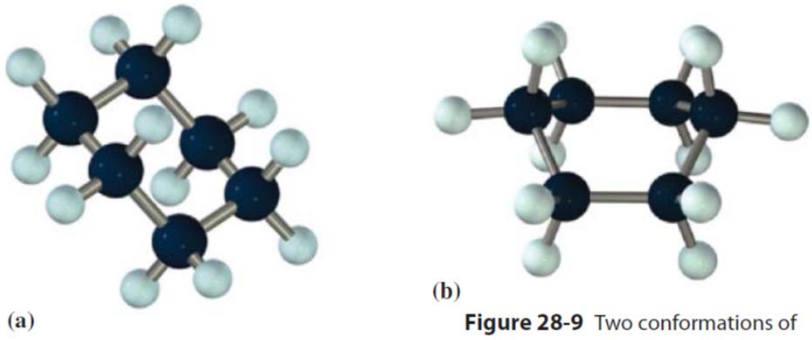
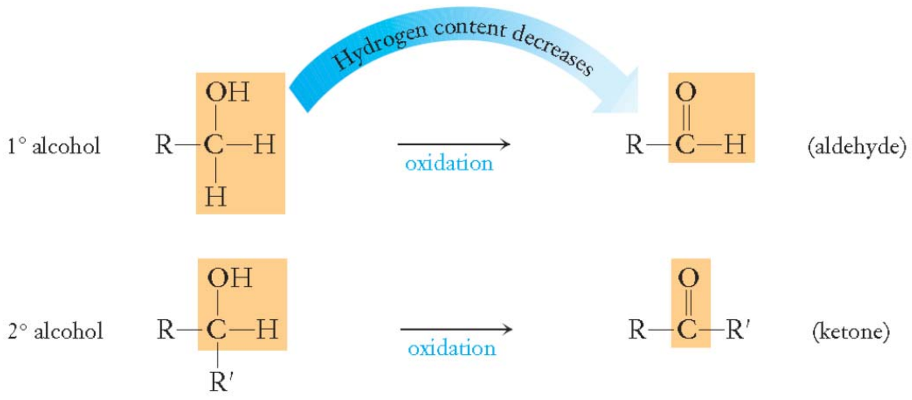
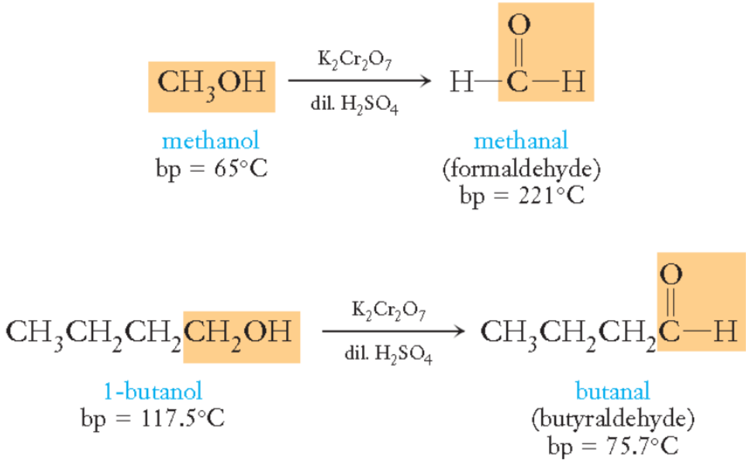


Figure 28-9 Two conformations of cyclohexane. (a) Chair and (b) boat.

Oxidation of alcohols



Oxidation of alcohols: primary



Oxidation of alcohols: secondary