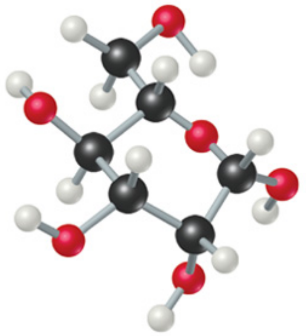
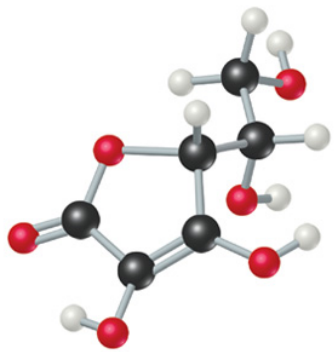
Chapter 24/25 Organic and Biological Chemistry

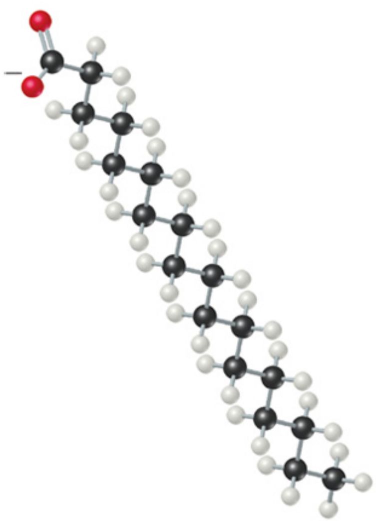
Organic Chemistry



Glucose ($C_6H_{12}O_6$)



Ascorbic acid ($HC_6H_7O_6$)

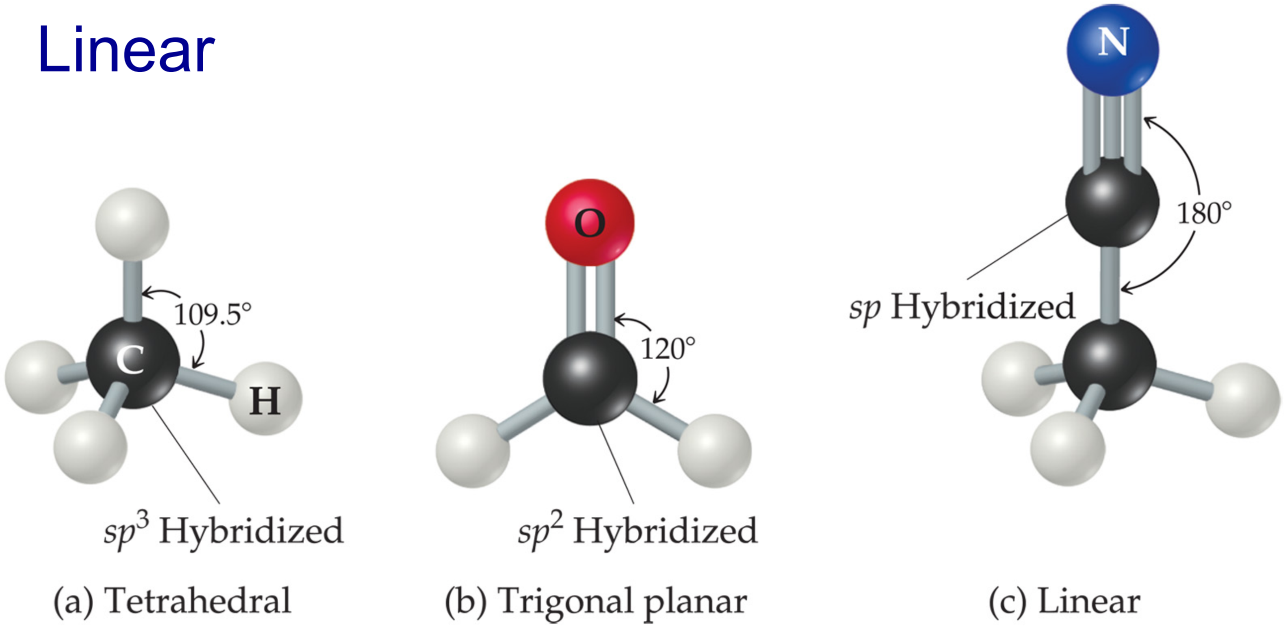


Surfactant ($C_{17}H_{35}COO^-$)

- The chemistry of carbon compounds.
- What's special about carbon?
  - tetravalent (sp^3 hybridization)
  - wide choice in oxidation states
  - CO_2 C, +4
  - CH_4 C, -4
  - bonds well to O,N,halides,itself,etc.
  - Covalent bonds are very strong

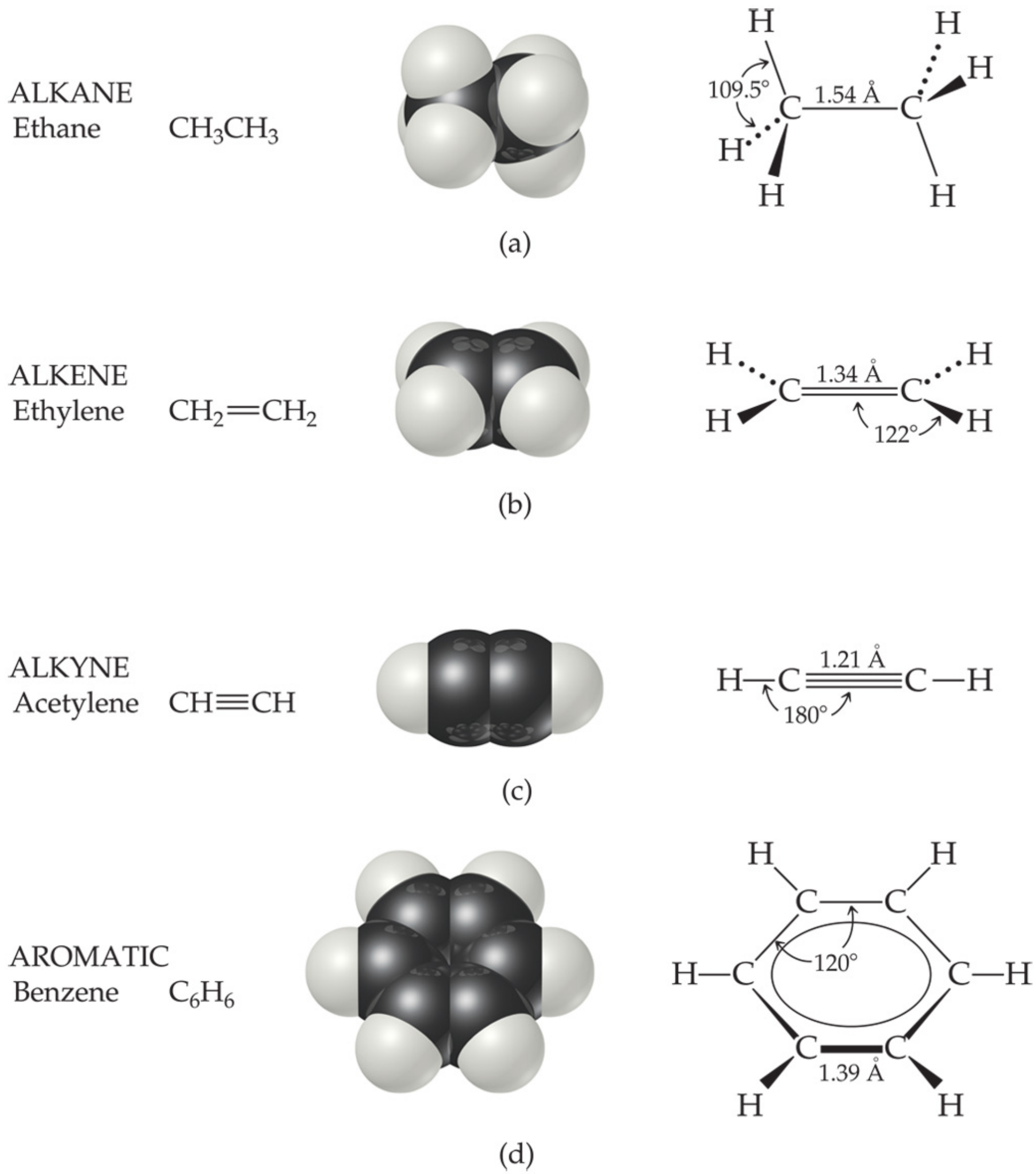
Structure of Carbon Compounds

- There are three hybridization states and geometries found in organic compounds:
  - *sp*^{3} Tetrahedral
  - *sp*^{2} Trigonal planar
  - *sp* Linear



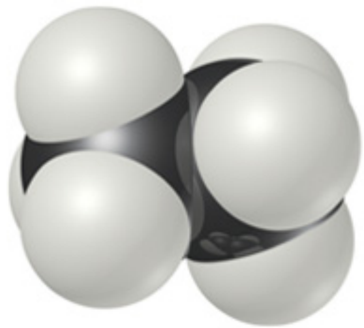
Hydrocarbons

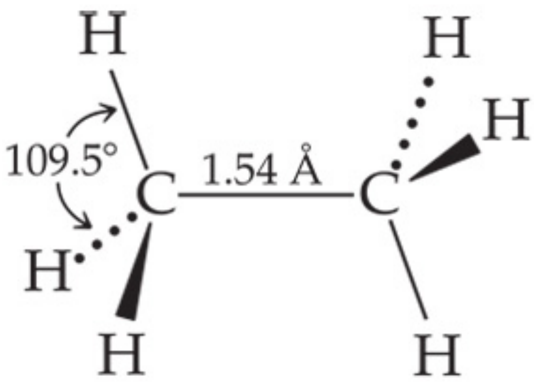
- Four types:
  - Alkanes
  - Alkenes
  - Alkynes
  - Aromatic hydrocarbons



Alkanes

ALKANE
Ethane CH_3CH_3

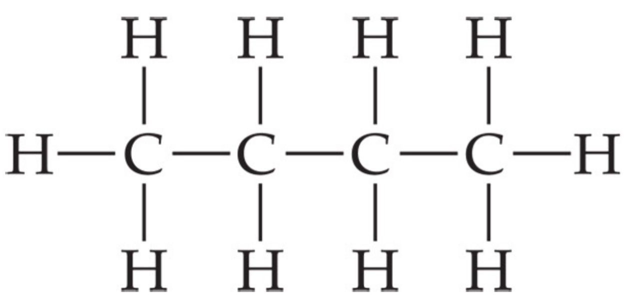




- Only single bonds.
- Saturated hydrocarbons.
  - “Saturated” with hydrogens.

Formulas

- Lewis structures of alkanes look like this.
- Also called structural formulas.
- Often not convenient, though…



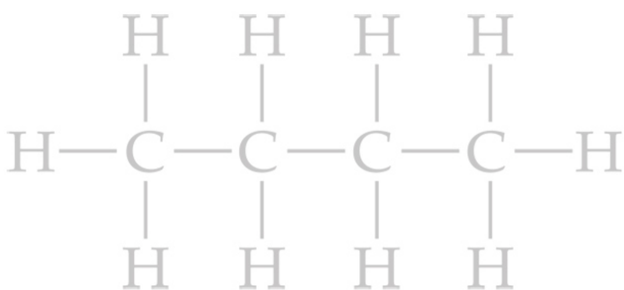
$$H_3C{-}CH_2{-}CH_2{-}CH_3$$

or

$$CH_3CH_2CH_2CH_3$$

Formulas

…so more often condensed formulas are used.

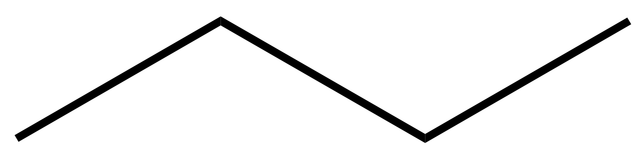


$H_3C—CH_2—CH_2—CH_3$

or

$CH_3CH_2CH_2CH_3$

or



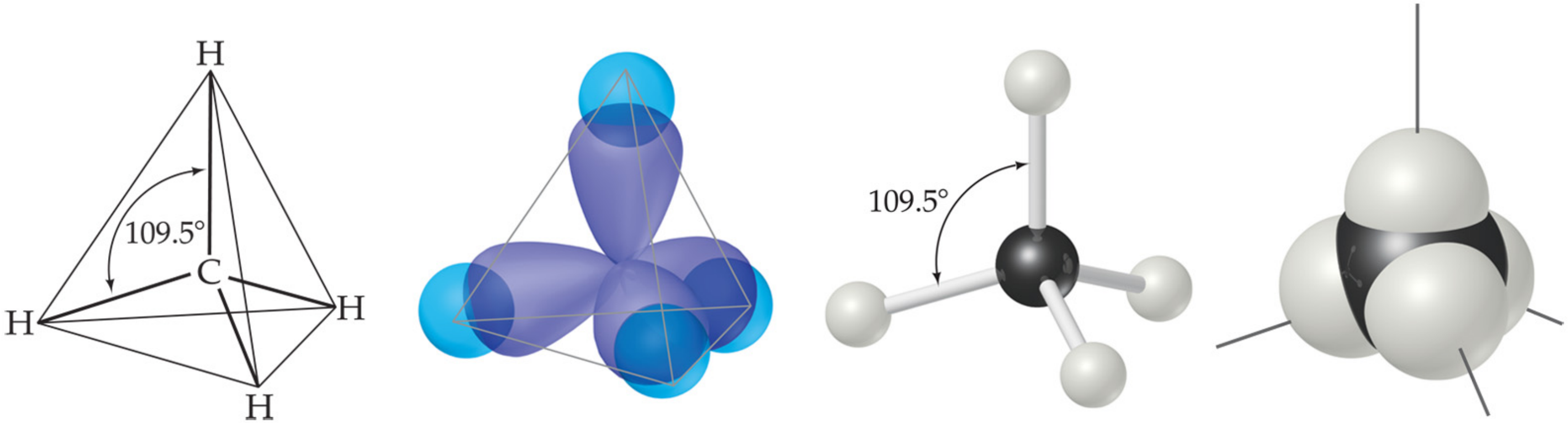
Note: always 4 *bonds to Carbon.*

Properties of Alkanes

Molecular Formula	Condensed Structural Formula	Name	Boiling Point (°C)
CH_4	CH_4	Methane	−161
C_2H_6	CH_3CH_3	Ethane	−89
C_3H_8	$CH_3CH_2CH_3$	Propane	−44
C_4H_{10}	$CH_3CH_2CH_2CH_3$	Butane	−0.5
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	Pentane	36
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane	68
C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	Heptane	98
C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Octane	125
C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Nonane	151
$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Decane	174

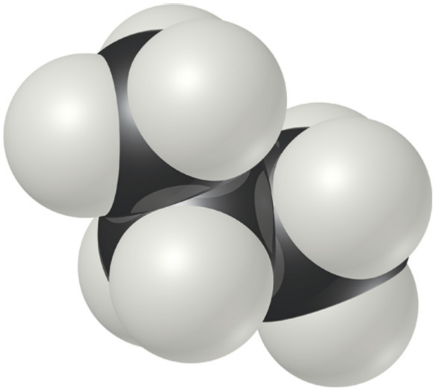
- Only van der Waals force: London force.
- Boiling point increases with length of chain.

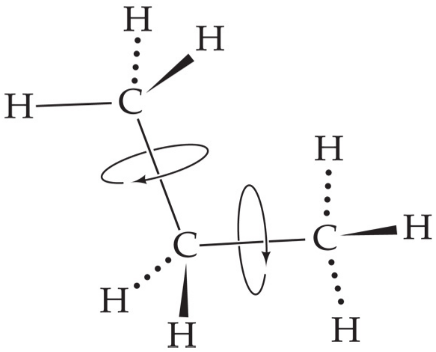
Structure of Alkanes



- Carbons in alkanes sp^3 hybrids.
- Tetrahedral geometry.
- 109.5° bond angles.

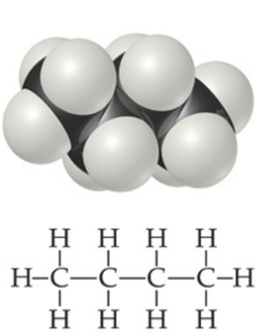
Structure of Alkanes





- Only σ-bonds in alkanes
- Free rotation about C—C bonds.

Isomers

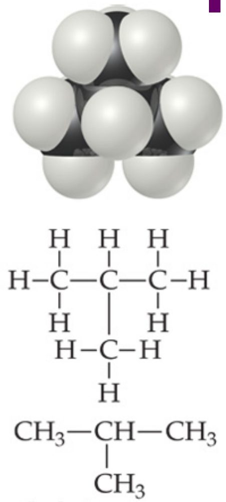


$CH_3CH_2CH_2CH_3$

Butane

mp −135° C

bp −0.5° C

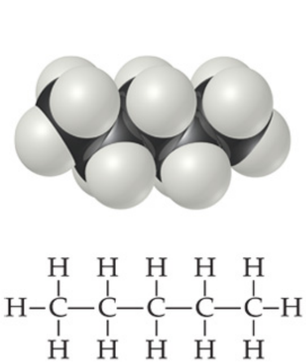


Isobutane

(2-methylpropane)

mp −145° C

bp −10° C

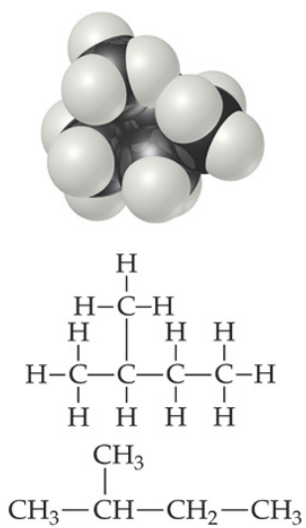


$CH_3CH_2CH_2CH_2CH_3$

Pentane

mp −130° C

bp +36°C

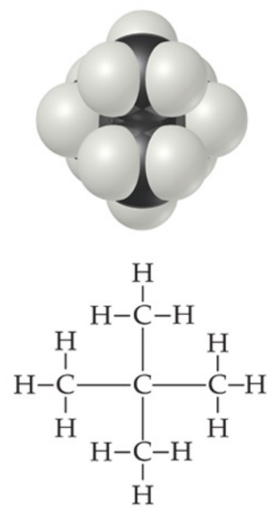


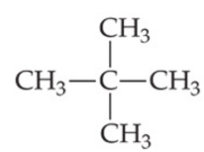
Isopentane

(2-methylbutane)

mp −160° C

bp +28° C





Neopentane

(2,2-dimethylpropane)

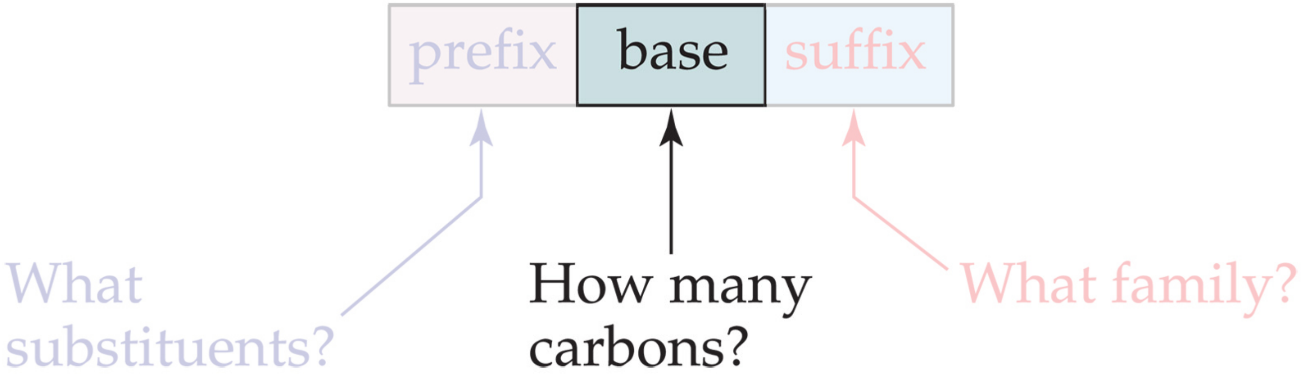
mp −20° C

bp +9° C

Have same molecular formulas, but atoms are bonded in different order.

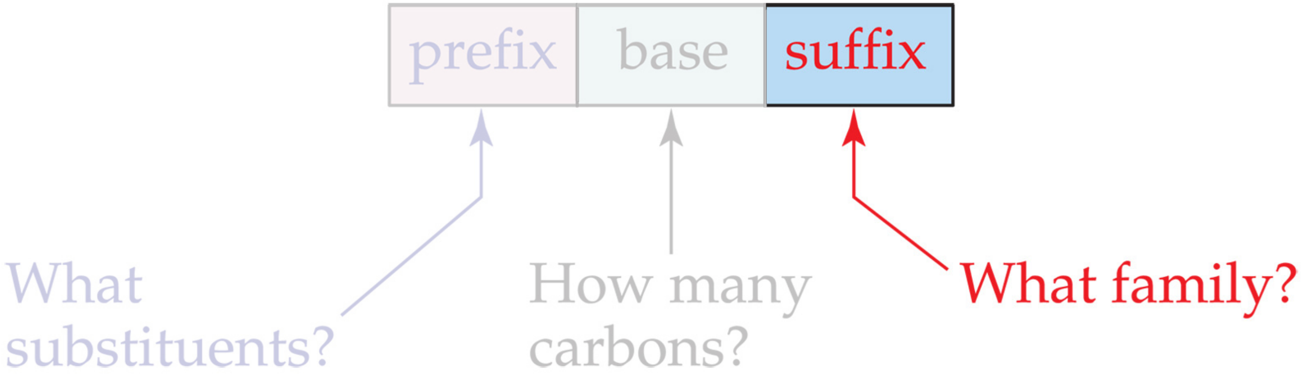
Organic Nomenclature

- Three parts to a compound name:
    - *Base*: Tells how many carbons are in the longest continuous chain.



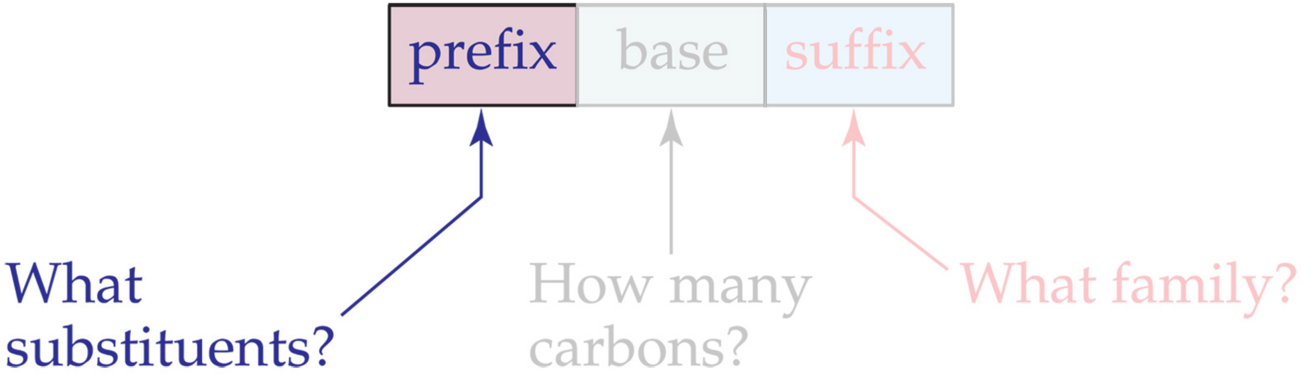
Organic Nomenclature

- Three parts to a compound name:
  - Base: Tells how many carbons are in the longest continuous chain.
  - Suffix: Tells what type of compound it is.

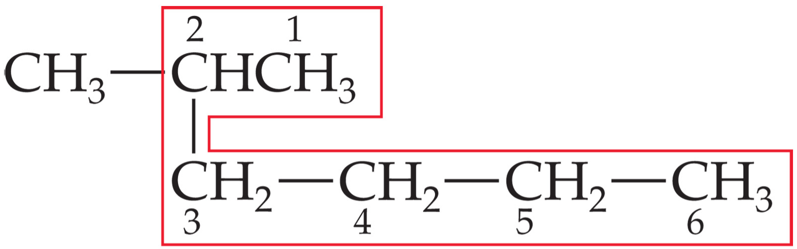


Organic Nomenclature

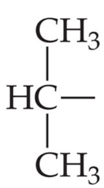
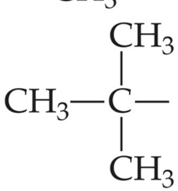
- Three parts to a compound name:
  - Base: Tells how many carbons are in the longest continuous chain.
  - Suffix: Tells what type of compound it is.
  - Prefix: Tells what groups are attached to chain.



To Name a Compound…

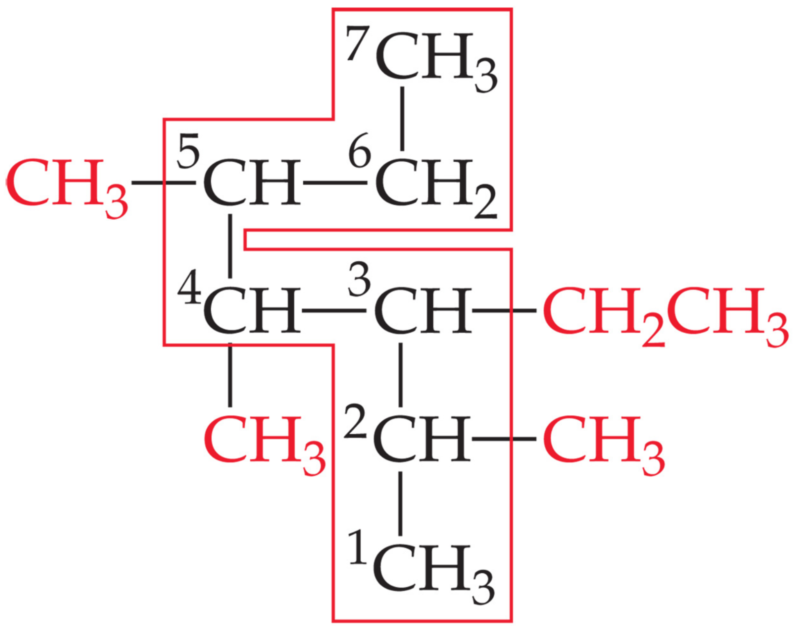


2-Methyl*hexane*

Group	Name
CH_3—	Methyl
CH_3CH_2—	Ethyl
$CH_3CH_2CH_2$—	Propyl
$CH_3CH_2CH_2CH_2$—	Butyl
	Isopropyl
	*tert*-Butyl

1. Find the longest chain in the molecule.
2. Number the chain from the end nearest the first substituent encountered.
3. List the substituents as a prefix along with the number(s) of the carbon(s) to which they are attached.

To Name a Compound…



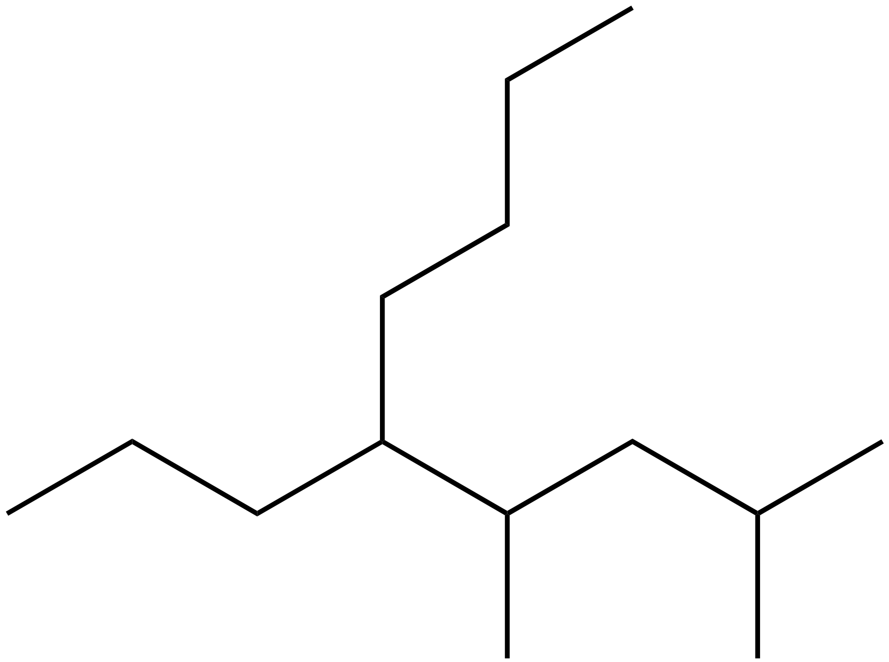
3-Ethyl-2,4,5-trimethylheptane

list substiutents alphabetically.

More than one longest chain:

pick the one with the most substituents.

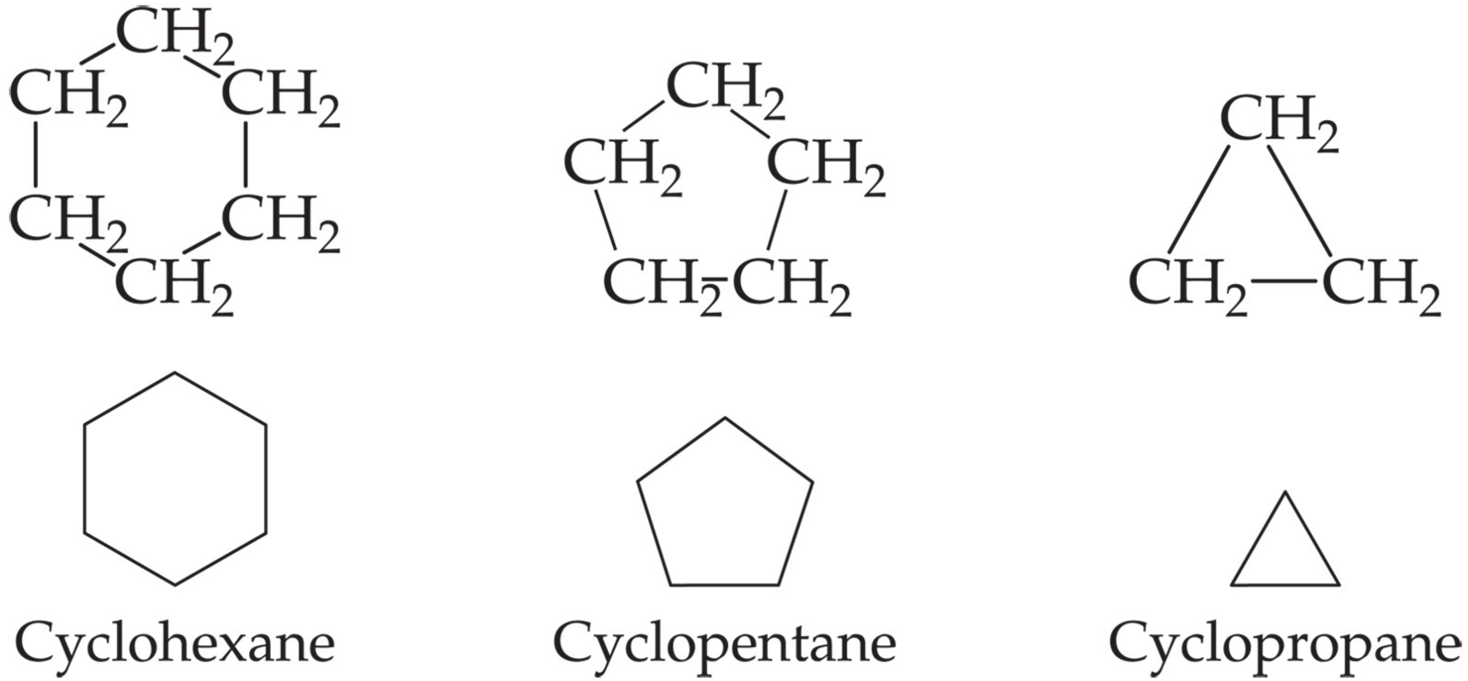
The most substituents:



2,4-dimethyl-5-propylnonane

Cycloalkanes

- Carbon can also form ringed structures.
- Five- and six-membered rings are most stable.
  - Can take on conformation in which angles are very close to tetrahedral angle.
  - Smaller rings are quite strained.

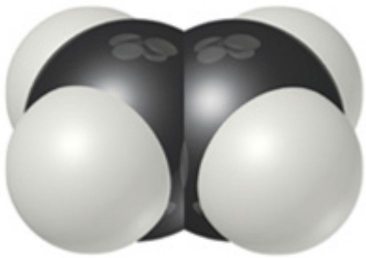


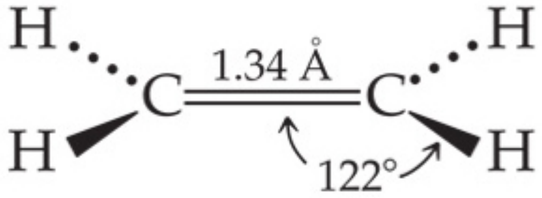
Reactions of Alkanes

- Rather unreactive due to presence of only C—C and C—H σ-bonds.
- Therefore, great nonpolar solvents.
- General rule of organic chemistry;
  - reactivity comes from the **functional groups**, ie. the part of the molecule that is not just an alkane.
  - different functional groups give rise to different kinds of activity.

Alkenes

ALKENE
Ethylene $CH_2{=}CH_2$

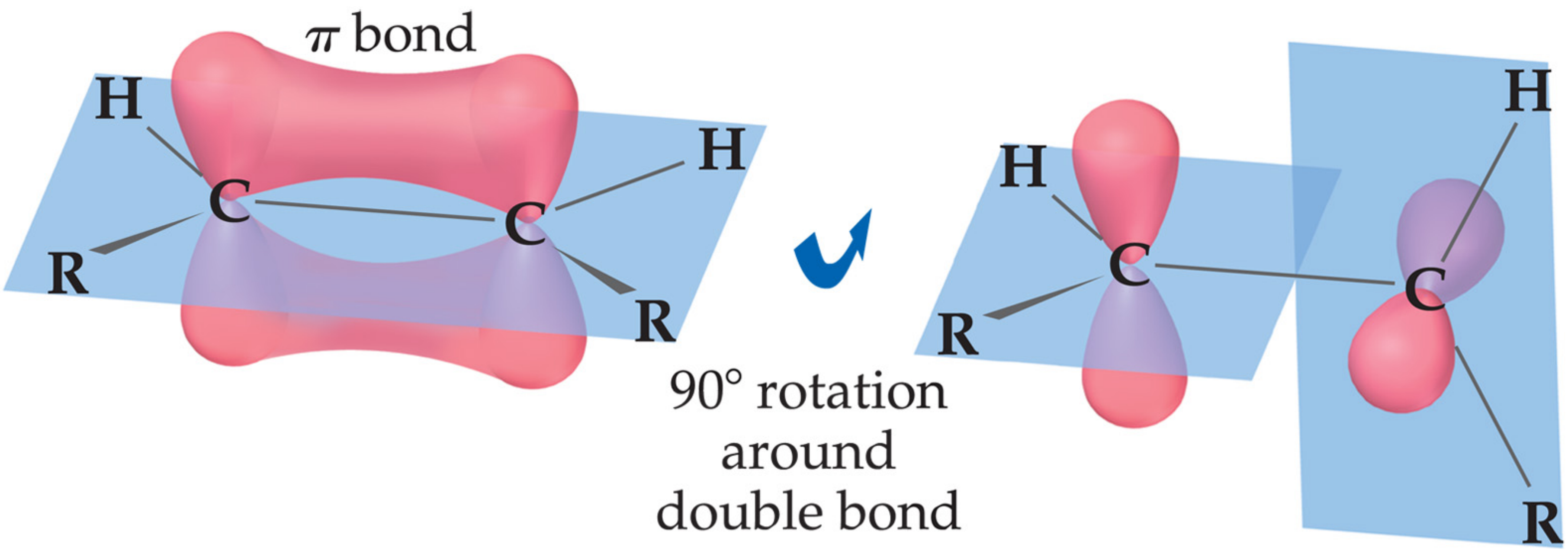




- Contain at least **one** carbon–carbon double bond.
- Unsaturated.
    - Have fewer than maximum number of hydrogens.

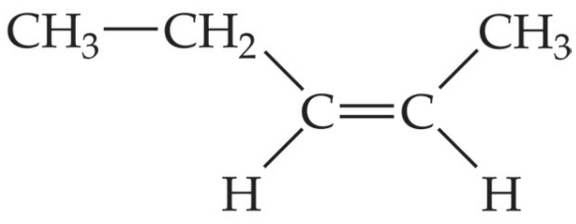
Structure of Alkenes

- Unlike alkanes, alkenes cannot rotate freely about the double bond.
  - **Side-to-side overlap makes this impossible without breaking π-bond.**

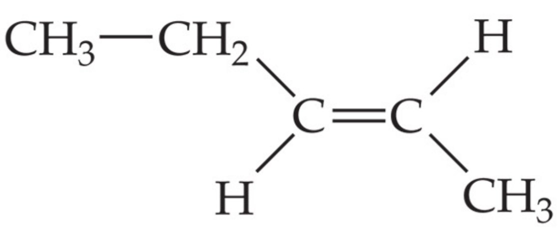


Structure of Alkenes

This creates geometric isomers, which differ from each other in the spatial arrangement of groups about the double bond.

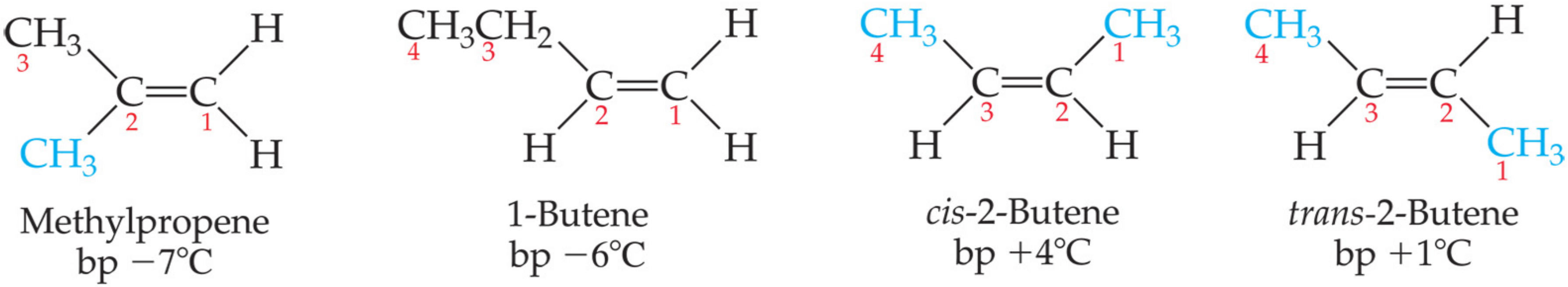


cis-2-Pentene



trans-2-Pentene

Properties of Alkenes

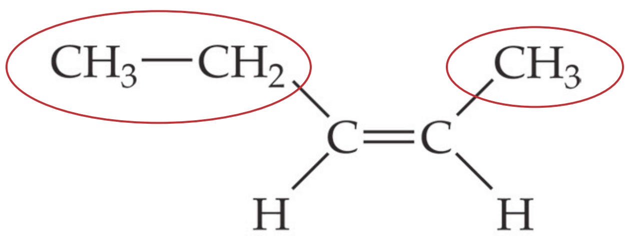


Structure also affects physical properties of alkenes.

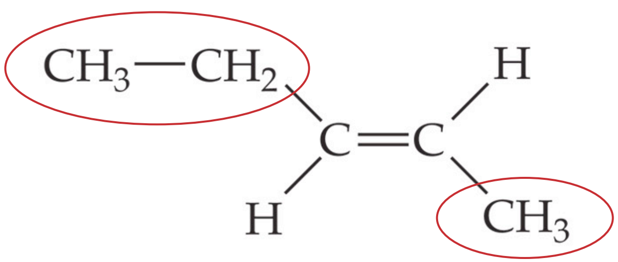
Nomenclature of Alkenes

- Chain numbered so double bond gets smallest possible number.
- *cis*- alkenes have ***carbons*** in chain on same side of molecule.
- *trans*- alkenes have carbons in chain on opposite side of molecule.

1-Pentene

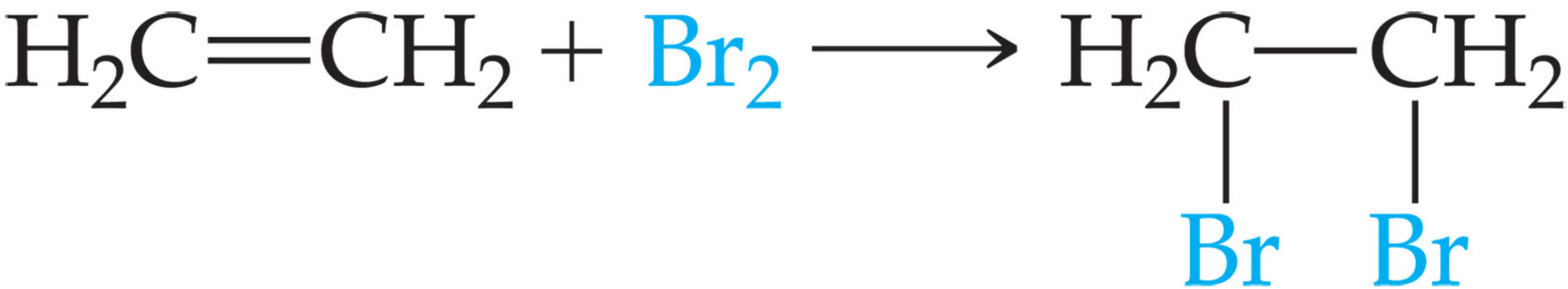


cis-2-Pentene



trans-2-Pentene

Reactions of Alkenes

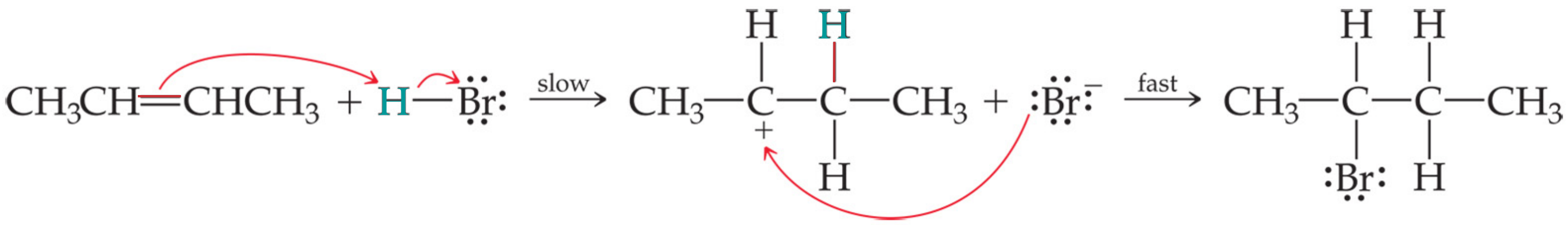


- Addition Reactions
  - Two atoms (e.g., bromine) add across the double bond.
  - One π-bond and one σ-bond are replaced by two σ-bonds; therefore, ΔH is negative.

“Arrow pushing

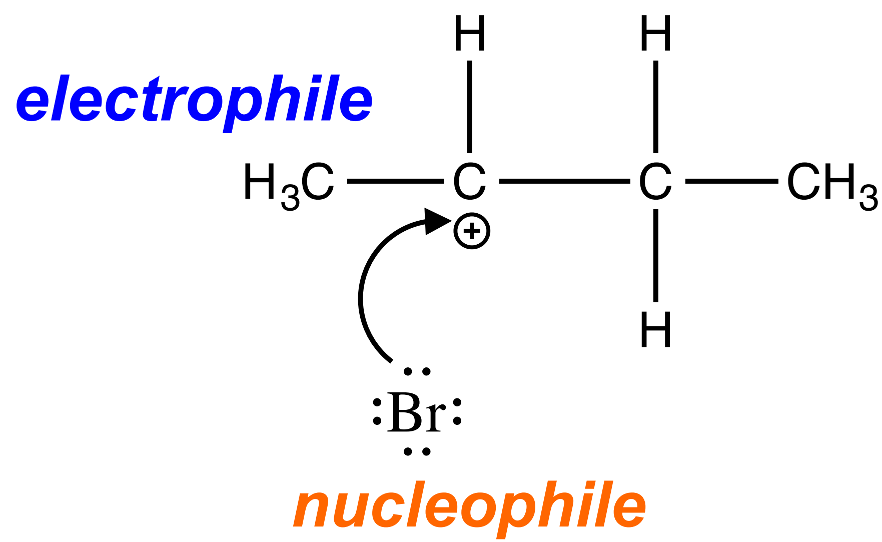
- The organic chemist’s language of reaction mechanism

Mechanism of Addition Reactions



- **The basics of arrow pushing:**
  - **Arrow goes from where electrons come from to where they are going.**
  - **Double headed arrow indicates 2 electrons**
  - **Single headed arrow indicates 1 electron**
- Alkene addition two-step mechanism:
  - First step is slow, rate-determining step.
  - Second step is fast.

Mechanism of Addition Reactions



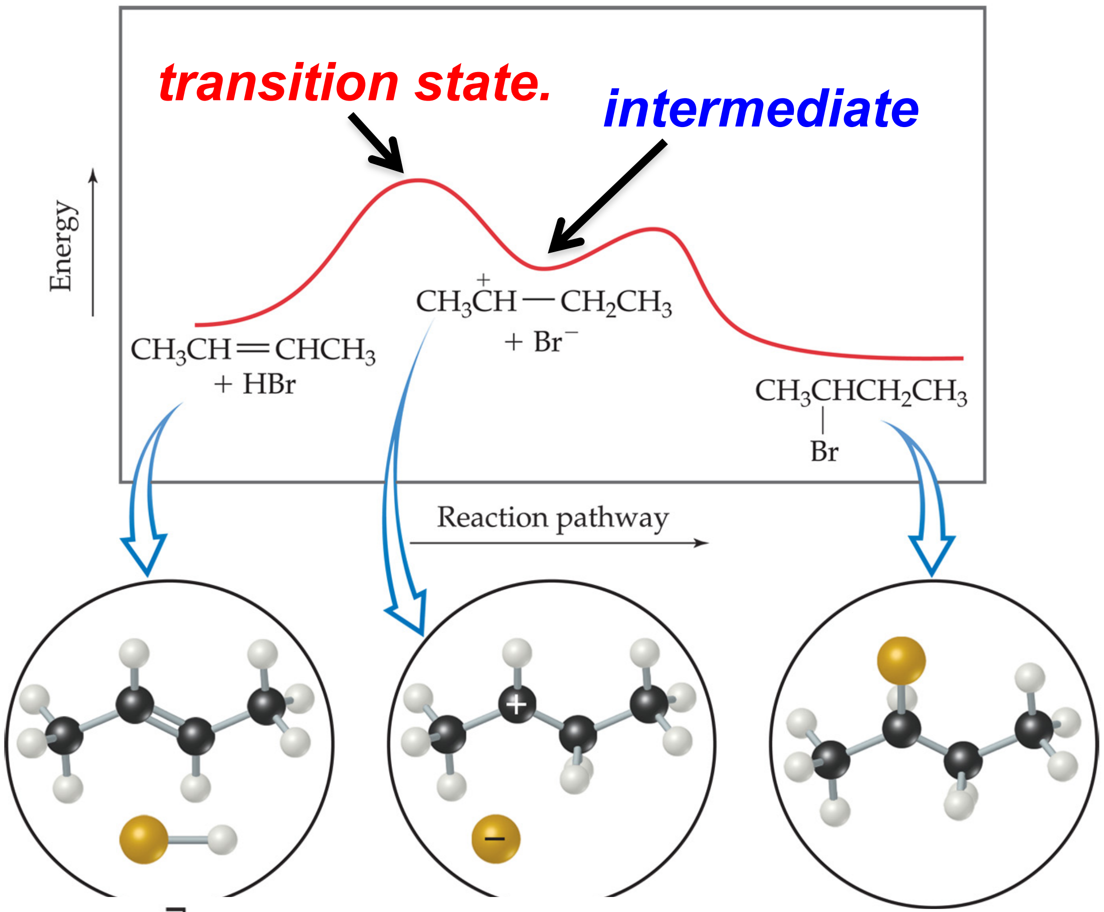
- **The basics of arrow pushing:**
  - **Arrow goes from where electrons come from to where they are going.**
  - **Double headed arrow indicates 2 electrons**
  - **Single headed arrow indicates 1 electron**
  - **Arrow goes from *nucleophile* to electrophile**

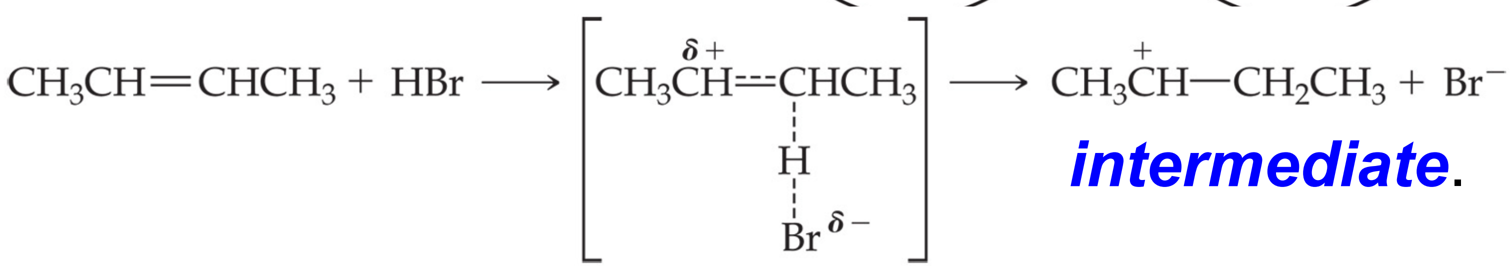
Mechanism of Addition Reactions

In first step, π-bond breaks and new C—H bond and cation form. An ***intermediate***.

The top of the hill:

a ***transition state.***





intermediate.

transition state.

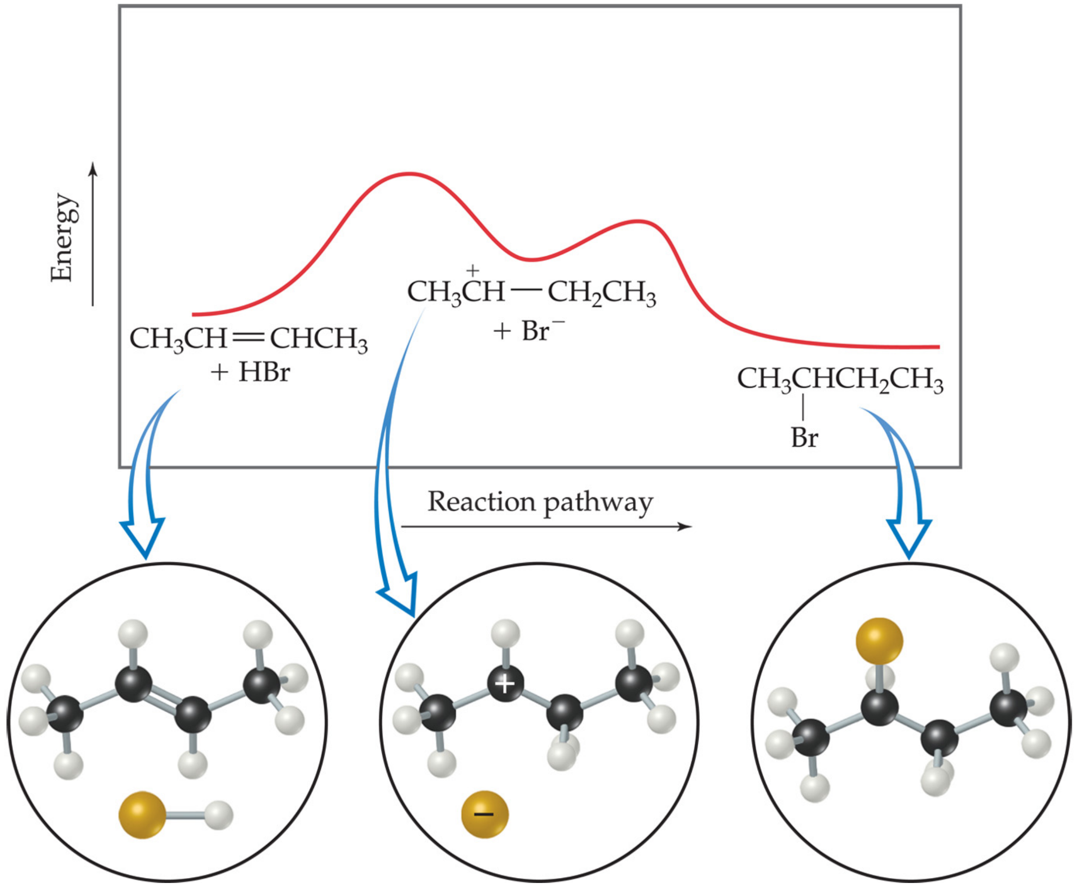
Mechanism of Addition Reactions

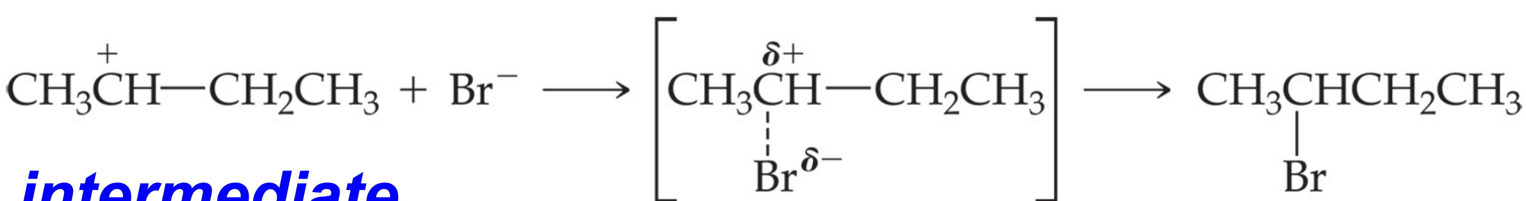
Valley in E diagram:

must be an intermediate!

Peak in E diagram:

Must be a transition state!



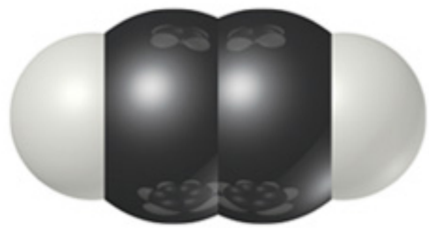


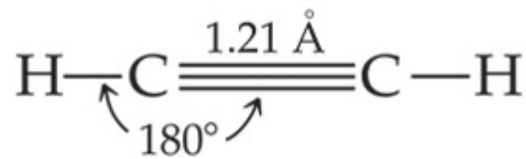
intermediate

Transition state

Alkynes

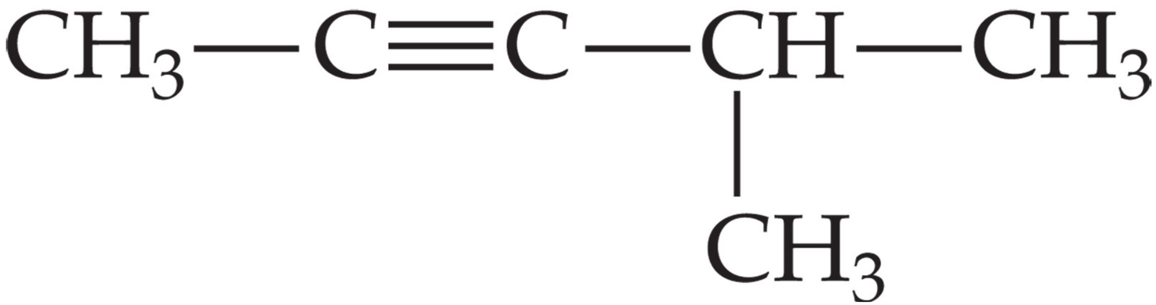
ALKYNE
Acetylene $CH{\equiv}CH$





- Contain at least one carbon–carbon triple bond.
- Carbons in triple bond *sp*-hybridized and have linear geometry.
- Also unsaturated.

Nomenclature of Alkynes

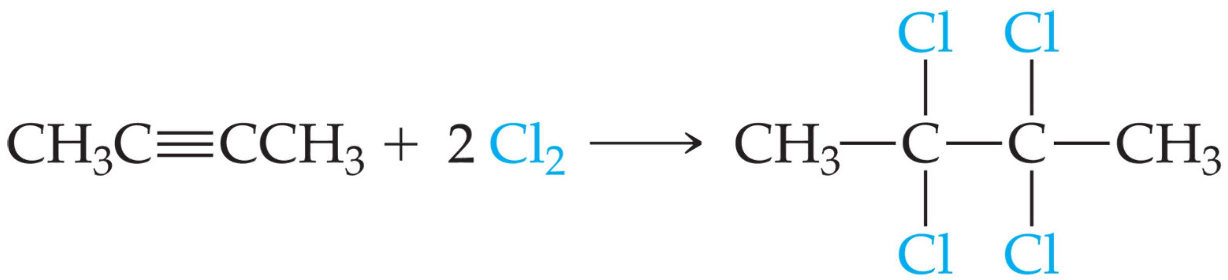


4-methyl-2-pentyne

- Analogous to naming of alkenes.
- Suffix is *-yne* rather than *–ene.*

Reactions of Alkynes

- Undergo many of the same reactions alkenes do.
- As with alkenes, impetus for reaction is replacement of π-bonds with σ-bonds.

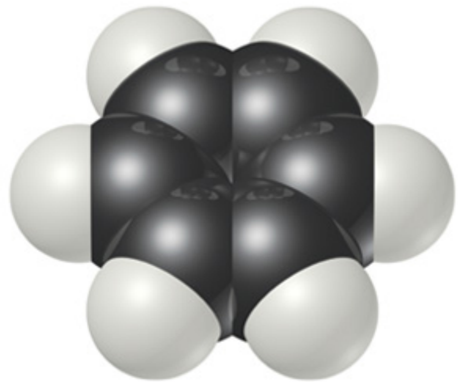


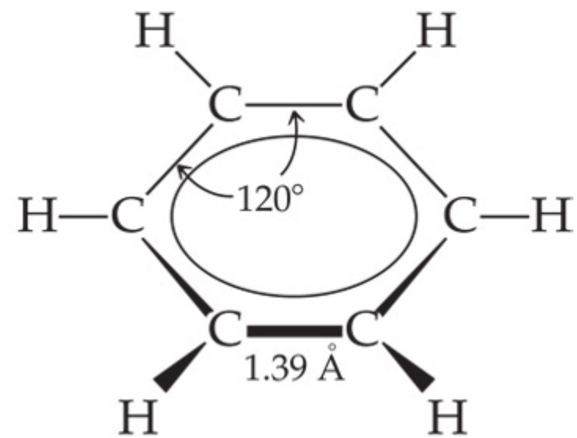
2-Butyne

2,2,3,3-Tetrachlorobutane

Aromatic Hydrocarbons

AROMATIC
Benzene C_6H_6



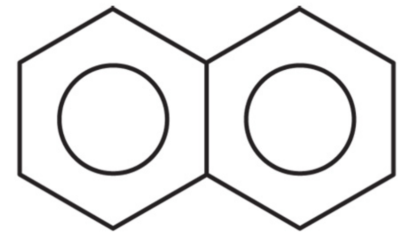


- Cyclic hydrocarbons.
- *p*-Orbital on each atom.
  - ➢ Molecule is planar.
- Odd number of electron pairs in π-system.
- 4n+2 pi electrons in a cycle.

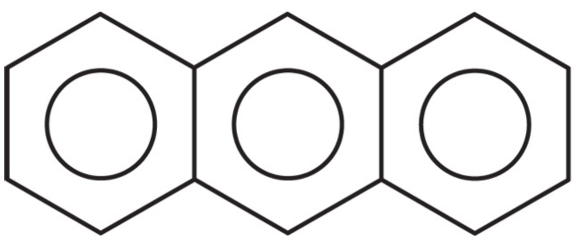
Aromatic Nomenclature

Many aromatic hydrocarbons are known by their common names.

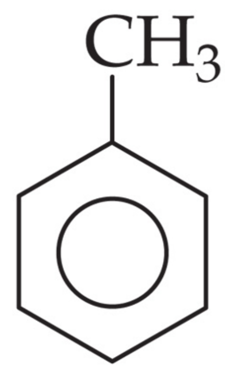
Benzene



Naphthalene

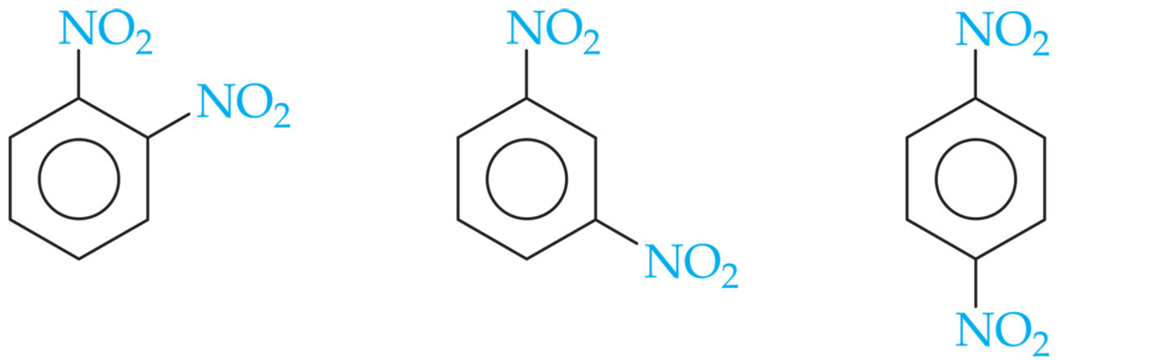


Anthracene



Toluene
Methylbenzene

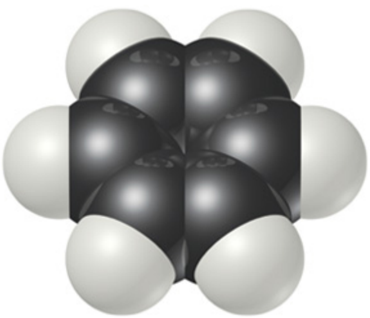
Structure of Aromatic Compounds

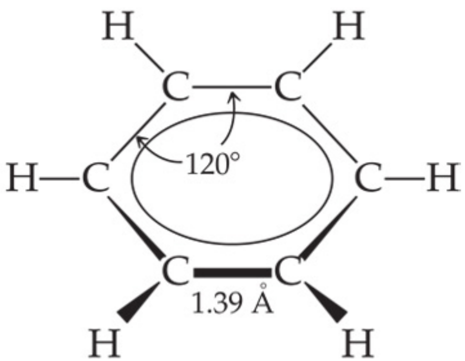


ortho-Dinitrobenzene mp 118°C | *meta*-Dinitrobenzene mp 90°C | *para*-Dinitrobenzene mp 174°C

- Two substituents on a benzene ring could have three possible relationships
  - *ortho-*: On adjacent carbons.
  - *meta-*: One carbon between them.
  - *para-*: On opposite sides of ring.

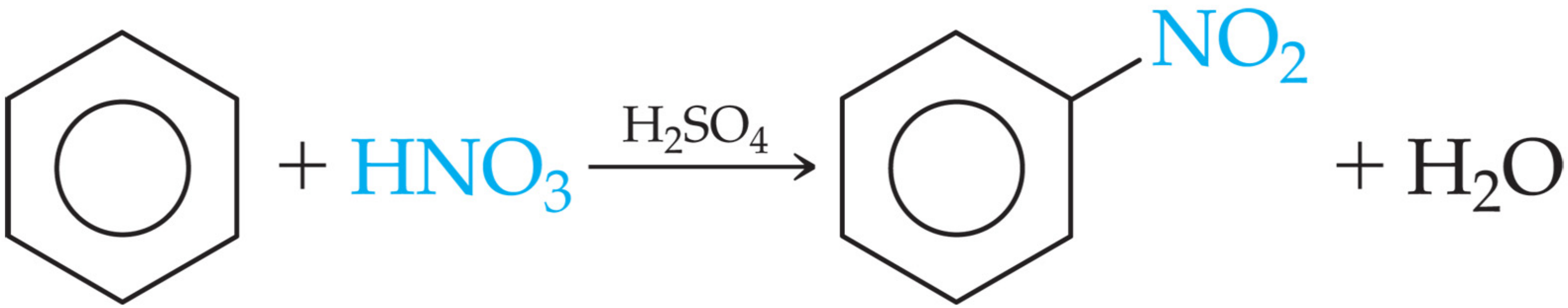
Reactions of Aromatic Compounds





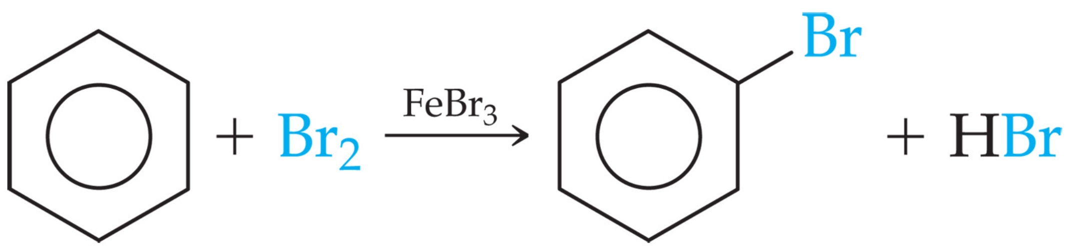
- Unlike in alkenes and alkynes, π-electrons do not sit between two atoms.
- Electrons are delocalized; this stabilizes aromatic compounds.

Reactions of Aromatic Compounds

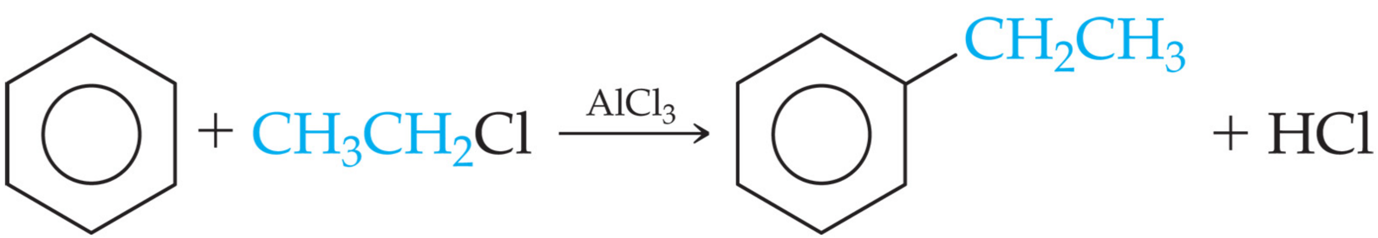


- Due to stabilization, aromatic compounds do not undergo addition reactions; they undergo substitution.
- Hydrogen is replaced by substituent.

Reactions of Aromatic Compounds



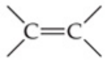
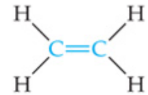
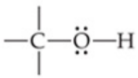
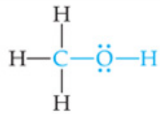
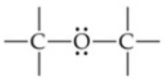
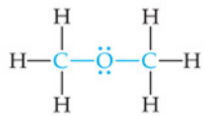
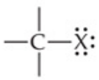
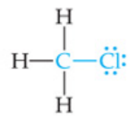
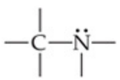
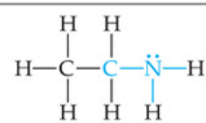
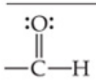
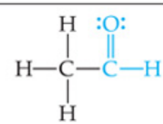
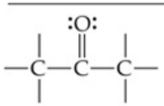
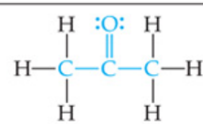
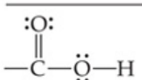
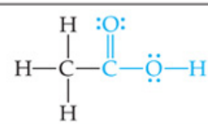
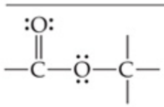
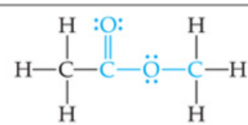
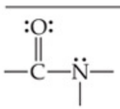
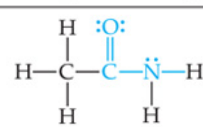
Halogenation



Friedel-Crafts Reaction

Reactions of aromatic compounds often require a catalyst.

Functional Groups

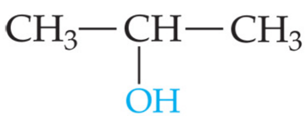
Functional Group	Type of Compound	Suffix or Prefix	Example	Systematic Name (common name)
	Alkene	*-ene*		Ethene (Ethylene)
	Alkyne	*-yne*		Ethyne (Acetylene)
	Alcohol	*-ol*		Methanol (Methyl alcohol)
	Ether	*ether*		Dimethyl ether
 (X = halogen)	Haloalkane	*halo-*		Chloromethane (Methyl chloride)
	Amine	*-amine*		Ethylamine
	Aldehyde	*-al*		Ethanal (Acetaldehyde)
	Ketone	*-one*		Propanone (Acetone)
	Carboxylic acid	*-oic acid*		Ethanoic acid (Acetic acid)
	Ester	*-oate*		Methyl ethanoate (Methyl acetate)
	Amide	*-amide*		Ethanamide (Acetamide)

The non alkane part of an organic molecule.

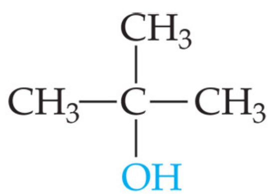
The more reactive part.

Alcohols

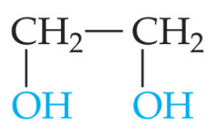
- Contain one or more hydroxyl groups, —OH
  - Named from parent hydrocarbon; suffix changed to *-ol* and number designates carbon to which hydroxyl is attached.



2-Propanol
Isopropyl alcohol; rubbing alcohol

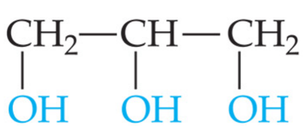


2-Methyl-2-propanol
t-Butyl alcohol

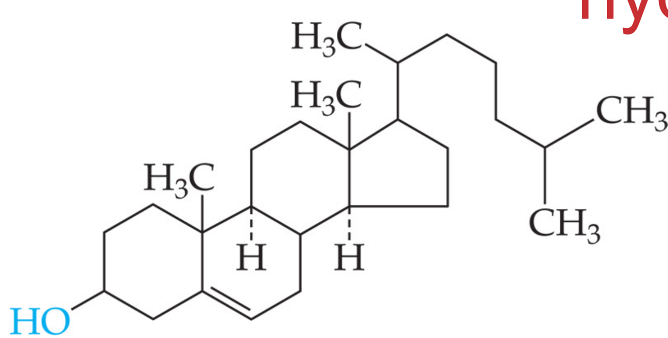


1,2-Ethanediol
Ethylene glycol

Phenol

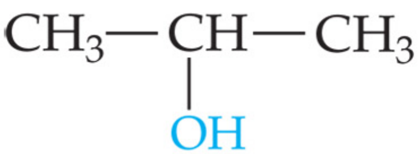


1,2,3-Propanetriol
Glycerol; glycerin

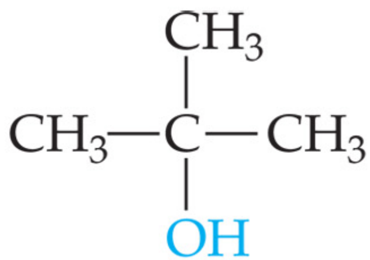


Cholesterol

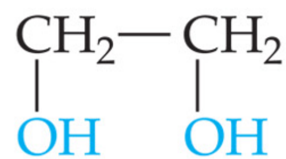
Alcohols



2-Propanol
Isopropyl alcohol; rubbing alcohol

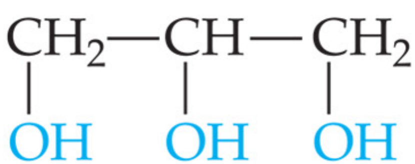


2-Methyl-2-propanol
t-Butyl alcohol

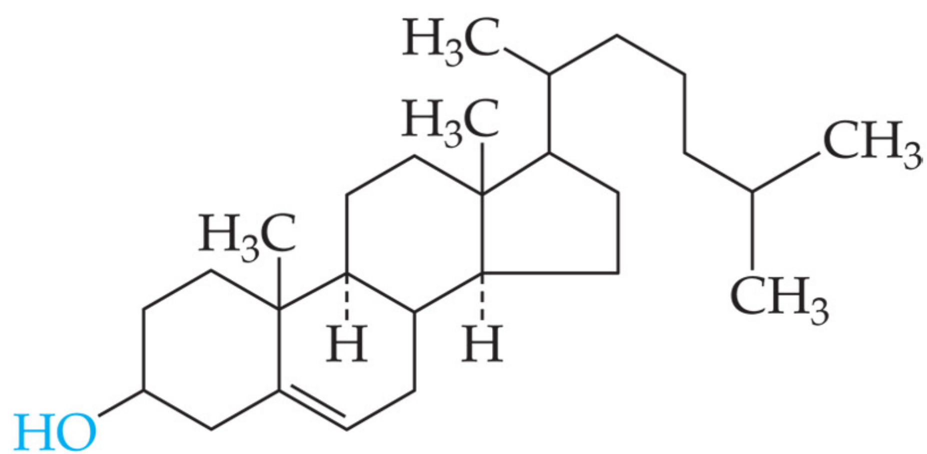


1,2-Ethanediol
Ethylene glycol

Phenol



1,2,3-Propanetriol
Glycerol; glycerin



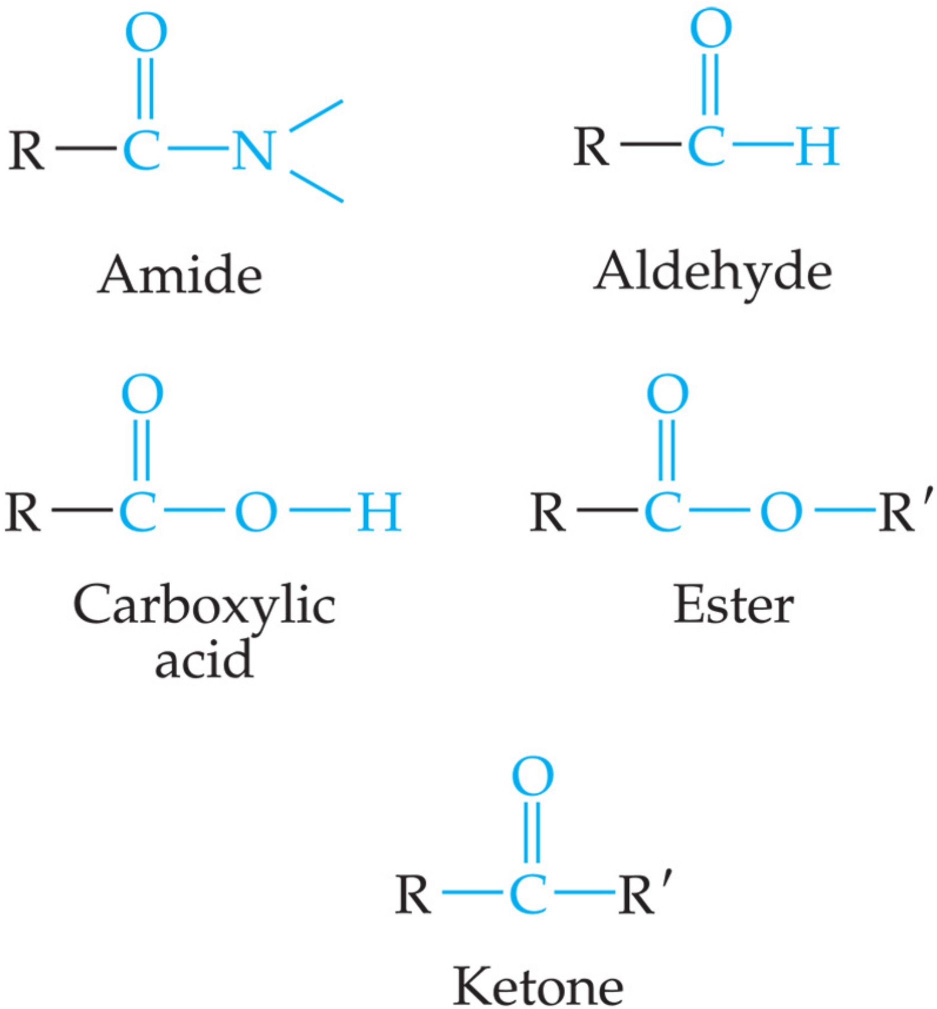
Cholesterol
a steroid

Ethers

$$CH_2{=}CH{-}O{-}CH{=}CH_2 \quad \text{(an anesthetic)}$$

- Tend to be quite unreactive.
- Therefore, they are good polar solvents.

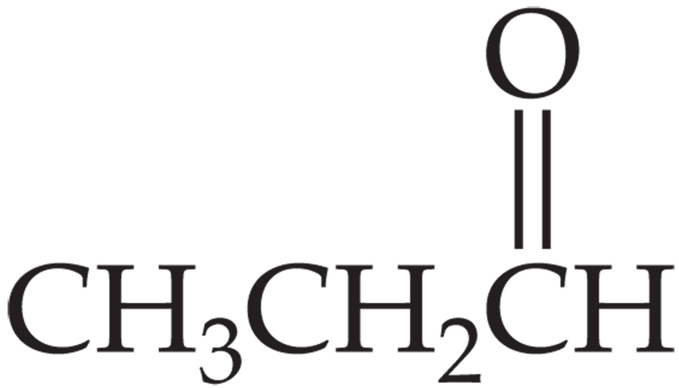
Carbonyl Compounds



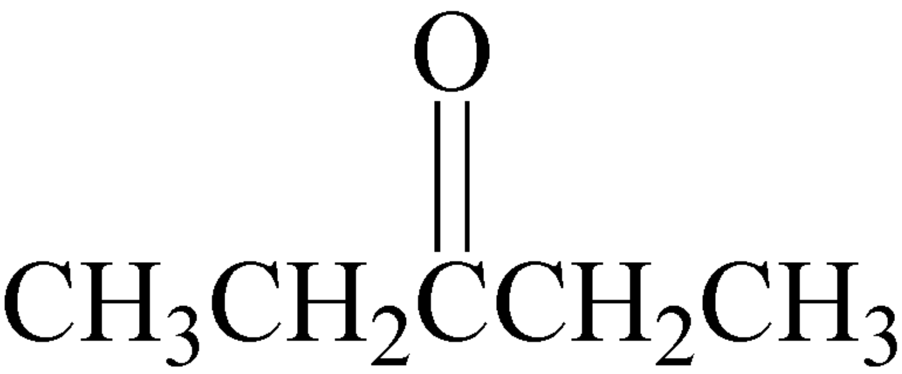
- Contain C—O double bond.
- Include many classes of compounds.

Aldehydes

At least one hydrogen attached to carbonyl carbon.



Ketones



Two carbons bonded to carbonyl carbon.

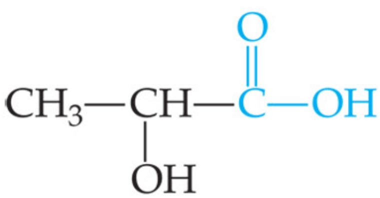
Carboxylic Acids

- Have hydroxyl group bonded to carbonyl group.
- Tart tasting.
- Carboxylic acids are weak acids .

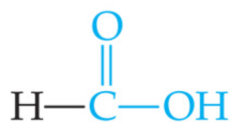
$$CH_3COOH$$

Acetic acid

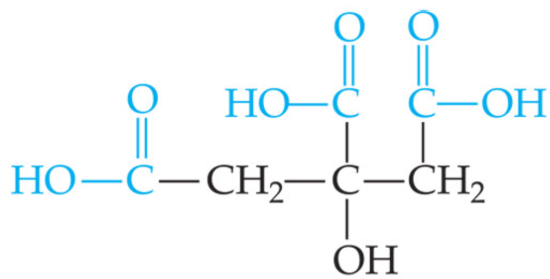
Carboxylic Acids



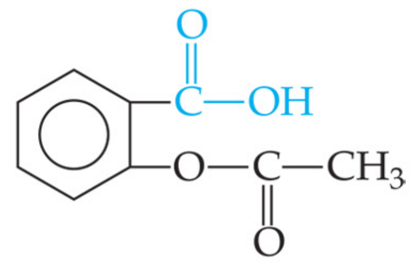
Lactic acid



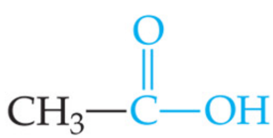
Methanoic acid
Formic acid



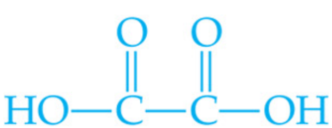
Citric acid



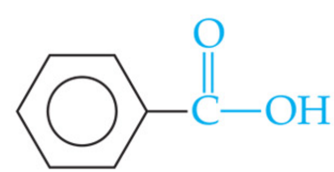
Acetylsalicylic acid
Aspirin



Ethanoic acid
Acetic acid

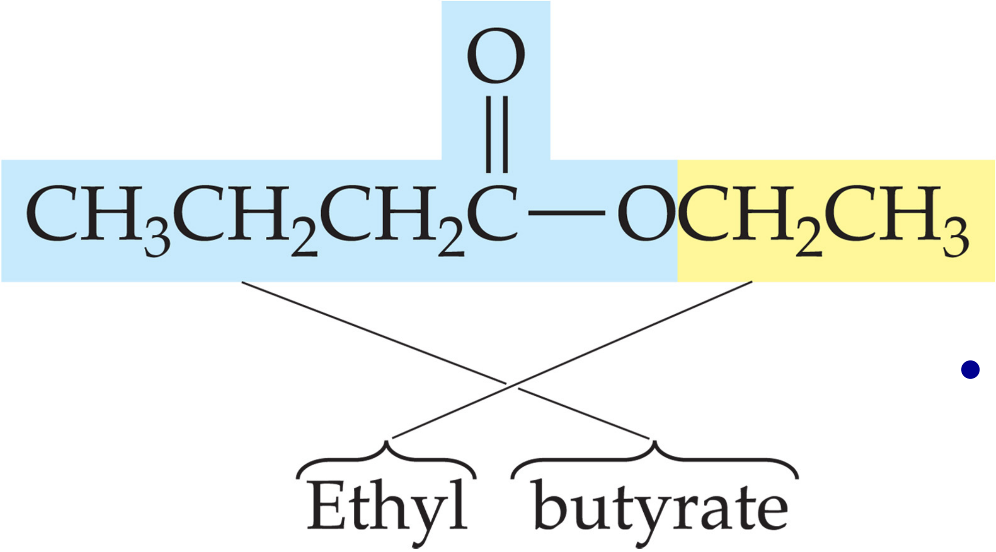


Oxalic acid



Phenyl methanoic acid
Benzoic acid

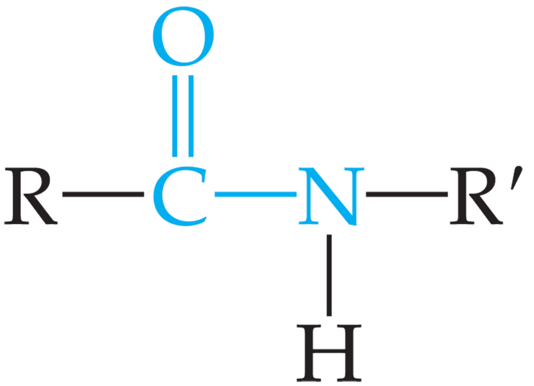
Esters



- Products of reaction between carboxylic acids and alcohols.
- Found in many fruits and perfumes.

Amides

Formed by reaction of carboxylic acids with amines.



Amines

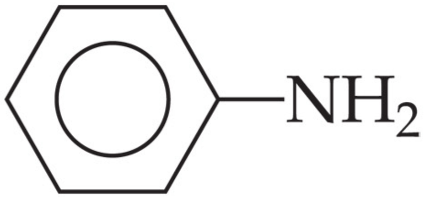
- Organic bases.
- Generally have strong, unpleasant odors.

$CH_3CH_2NH_2$

Ethylamine

$(CH_3)_3N$

Trimethylamine



Phenylamine
Aniline

Exam 4 Topics

1. Valence bond theory
2. Molecular orbital theory
3. Coordination chemistry
4. Organic

Valence bond theory:

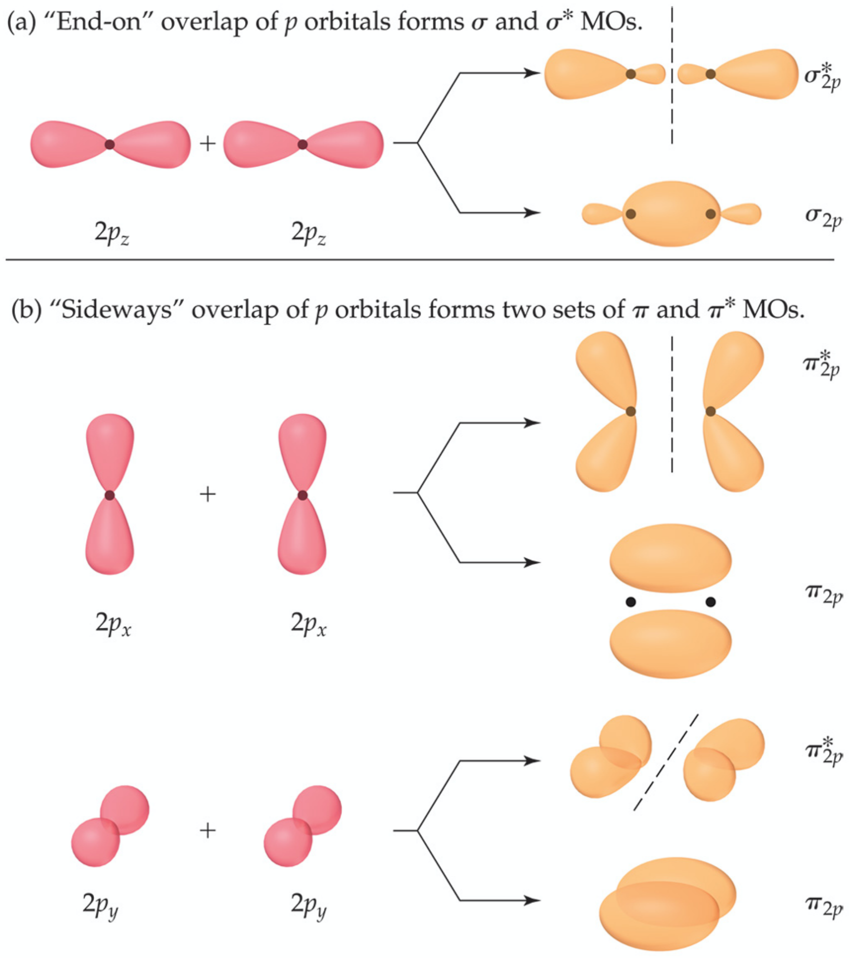
1. Hybridization (mostly covered in last exam)
2. Double bonds due to overlap of atomic p orbitals (pi bonds)
3. Concept of delocalization what orbitals are overlaping in a delocalized system?

Exam 4, MO theory and coordination compounds
Chapter 9, end and Chapter 24.

MO theory: Rules:

- 1. The number of MO's equals the # of Atomic orbitals
- 2. The overlap of two atomic orbitals gives two molecular orbitals, 1 bonding, one antibonding
- 3. Atomic orbitals combine with other atomic orbitals of *similar energy.*
- 4. Degree of overlap matters. More overlap means bonding orbital goes *lower* in E, antibonding orbital goes *higher* in E.
- 5. Each MO gets two electrons
- 6. Orbitals of the *same energy* get filled 1 electron at a time until they are filled.

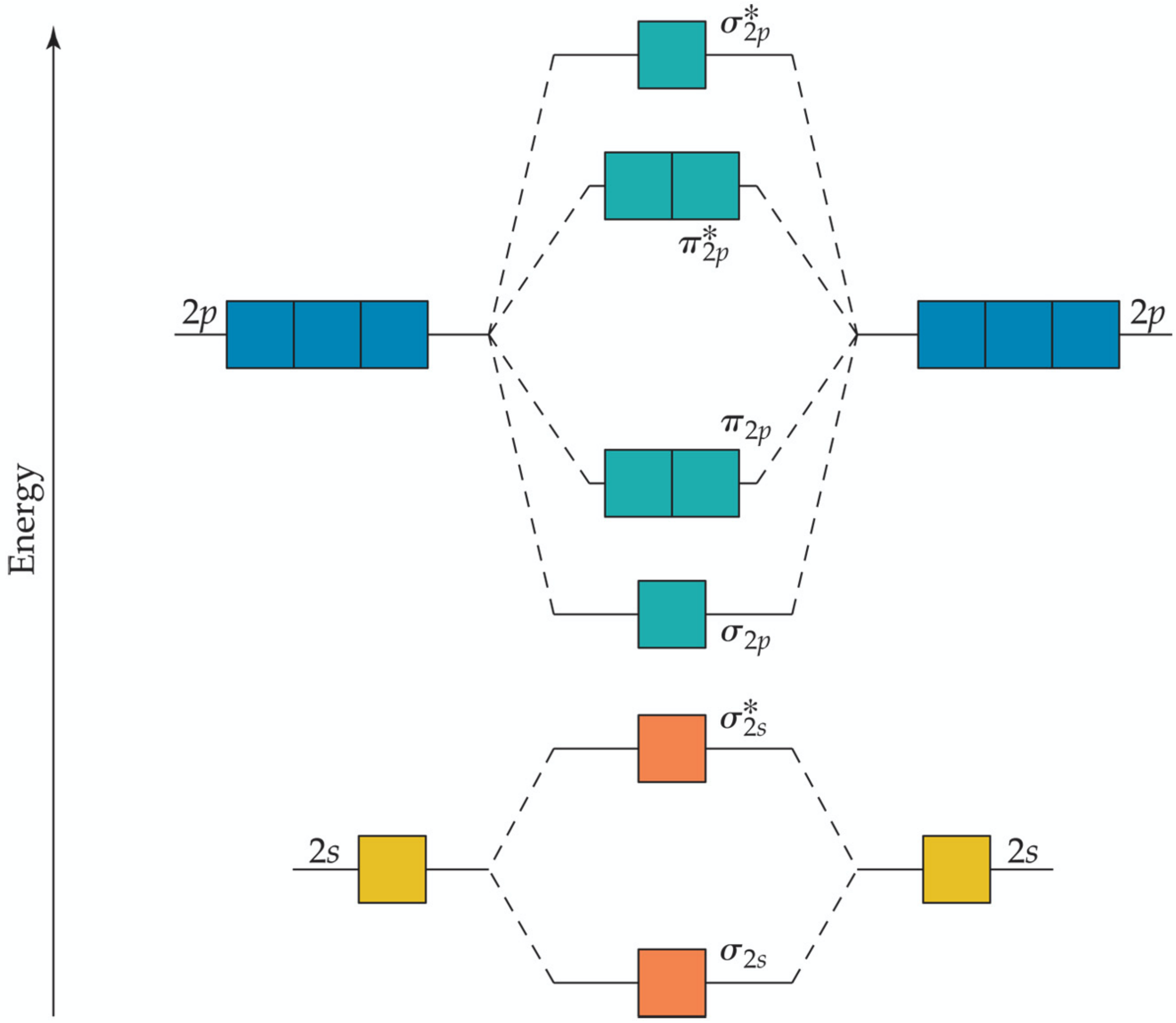
Difference between pi and sigma orbitals



End on

Side to side.

A typical MO diagram, like the one below.



Filling MO diagrams. Bond order etc.

	Large 2*s*-2*p* interaction				Small 2*s*-2*p* interaction		
	B_2	**C_2**	**N_2**		**O_2**	**F_2**	**Ne_2**
σ^*_{2p}				σ^*_{2p}			↑↓
π^*_{2p}				π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}			↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓	↑↓
Bond order	1	2	3		2	1	0
Bond enthalpy (kJ/mol)	290	620	941		495	155	—
Bond length (Å)	1.59	1.31	1.10		1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic		Paramagnetic	Diamagnetic	—

Exam 4 Coordination compounds.

Terms and concepts:

1. Coordination sphere
2. Ligand
3. Coordination compound
4. Metal complex
5. Complex ion
6. Coordination
7. Coordination number

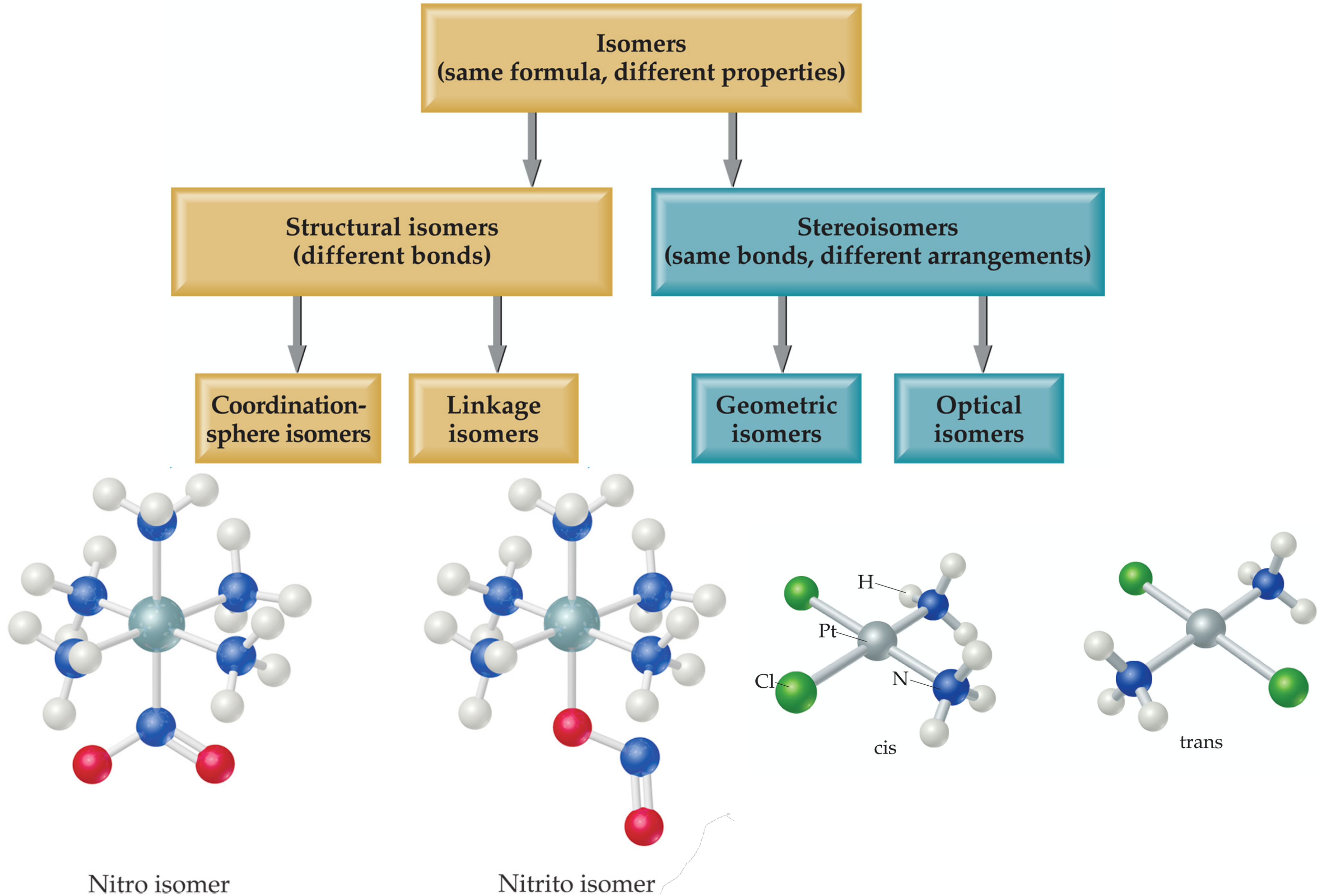
Same ligands different properties?

Figuring oxidation number on metal

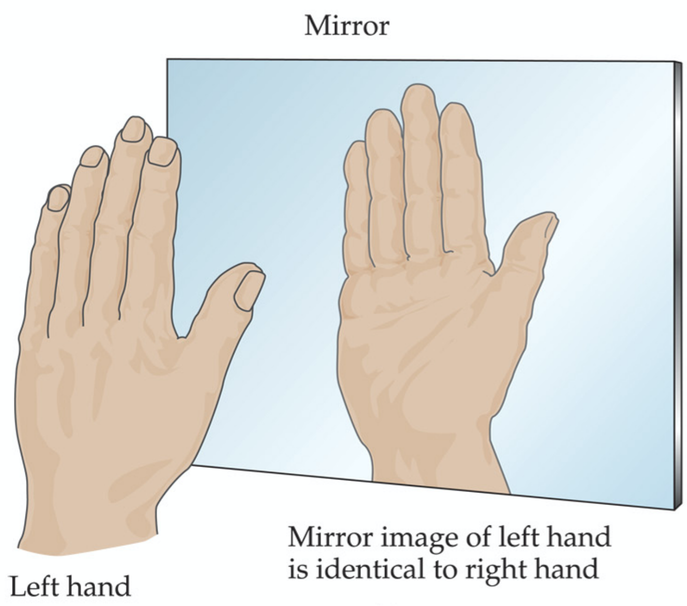
Polydentate ligands (what are they)?

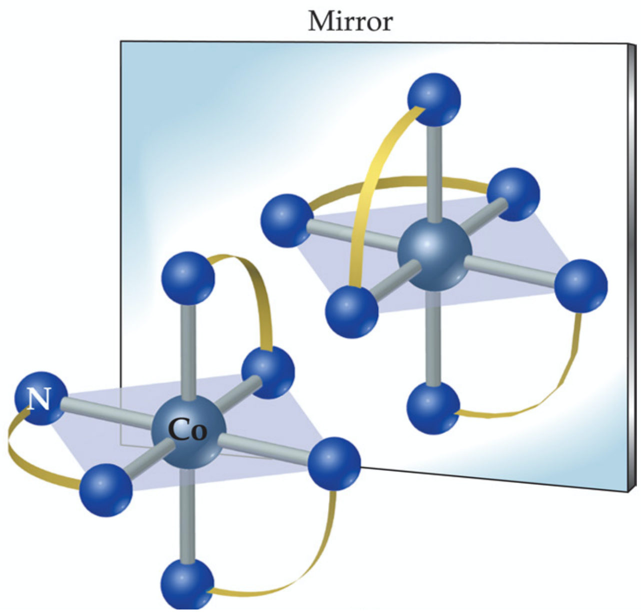
Isomers.

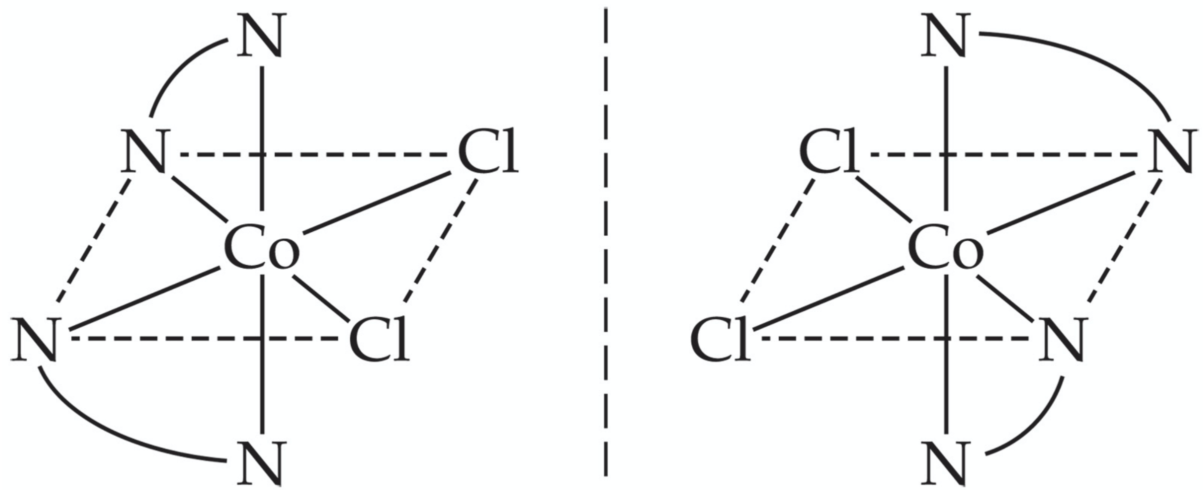
- structural isomers (formula same, bonds differ)
- geometric isomers (formula AND bonds same, structure differs)
  - Stereoisomers:
    - Chirality, handedness,


Isomers
(same formula, different properties)
Structural isomers
(different bonds)
Stereoisomers
(same bonds, different arrangements)
Coordination-sphere isomers
Linkage isomers
Geometric isomers
Optical isomers
H
Pt
Cl
N
cis
trans
Nitro isomer
Nitrito isomer

Stereoisomers







Explaining the properties of metal complexes

Magnetism and color

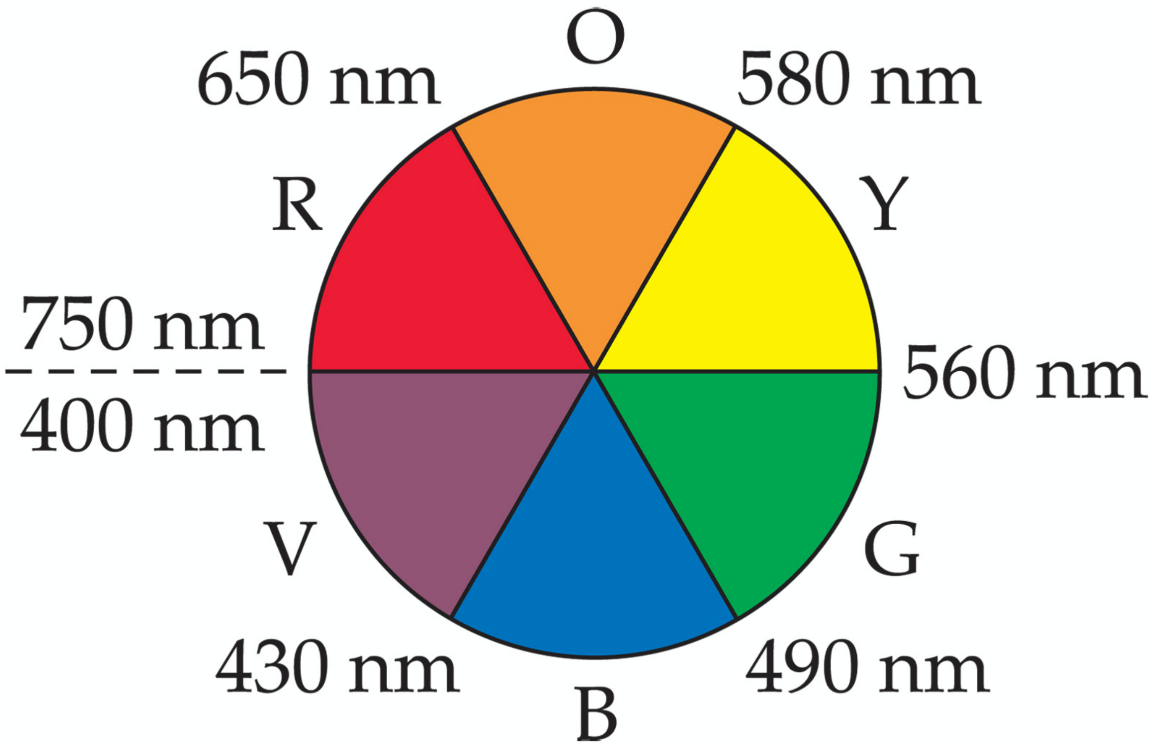
How does seeing color work?

Absorb **Orange**

See **Blue**

Absorb **Red**

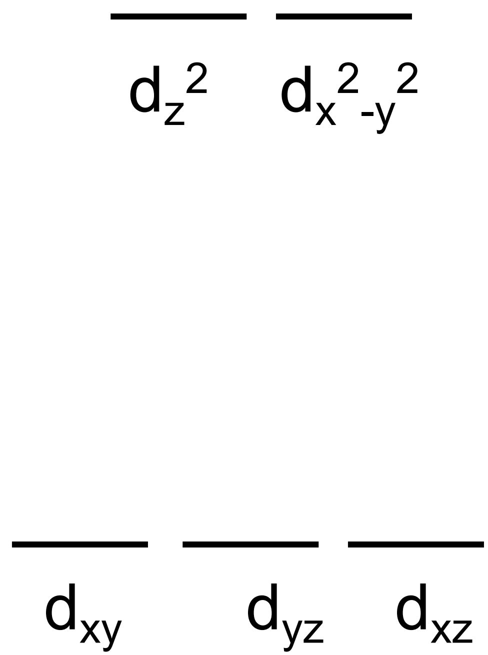
See **Green**



Different ligands on same metal give different colors

Addition of NH_3 ligand to $Cu(H_2O)_4$ changes its color

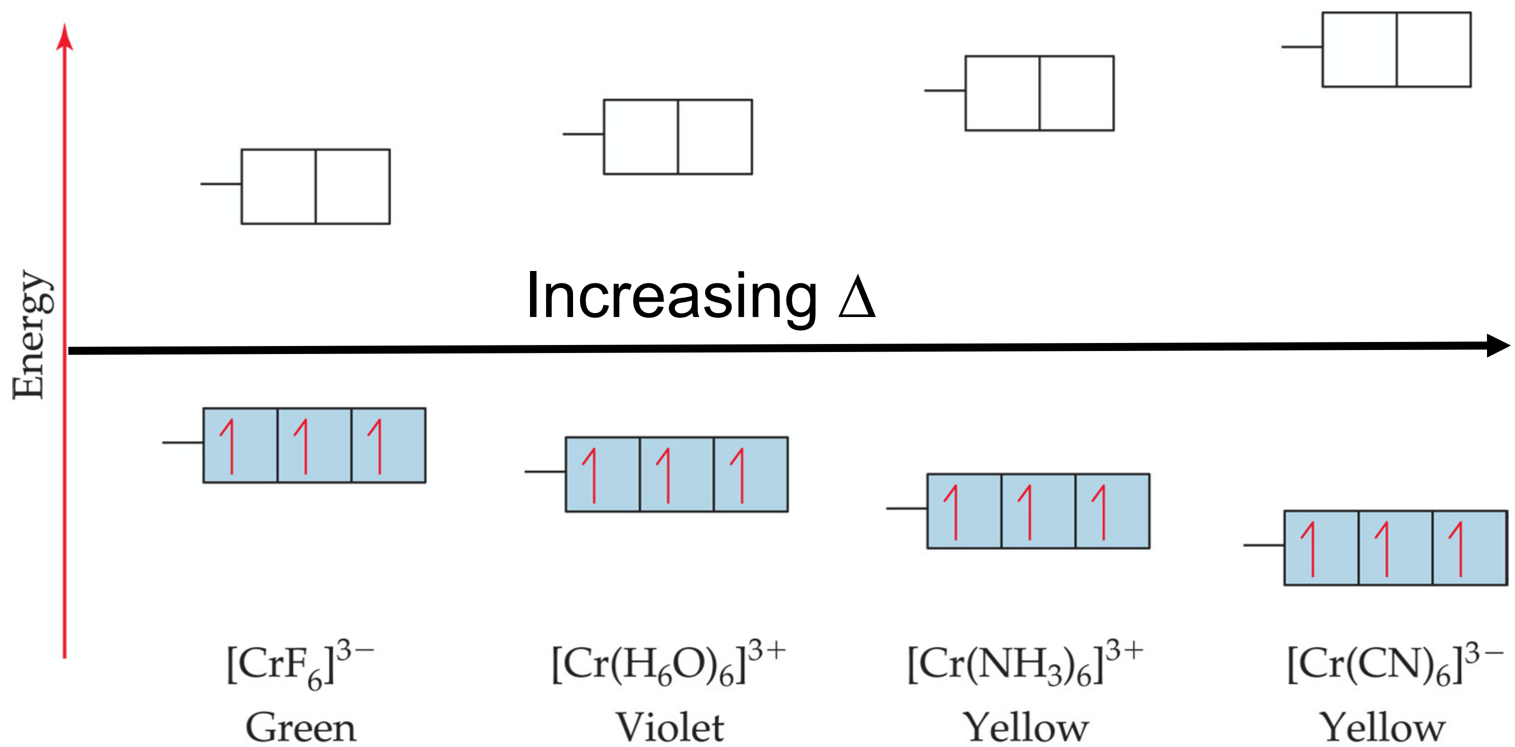
Splitting of d orbitals in an octahedral ligand field



Spectrochemical series (strength of ligand interaction)

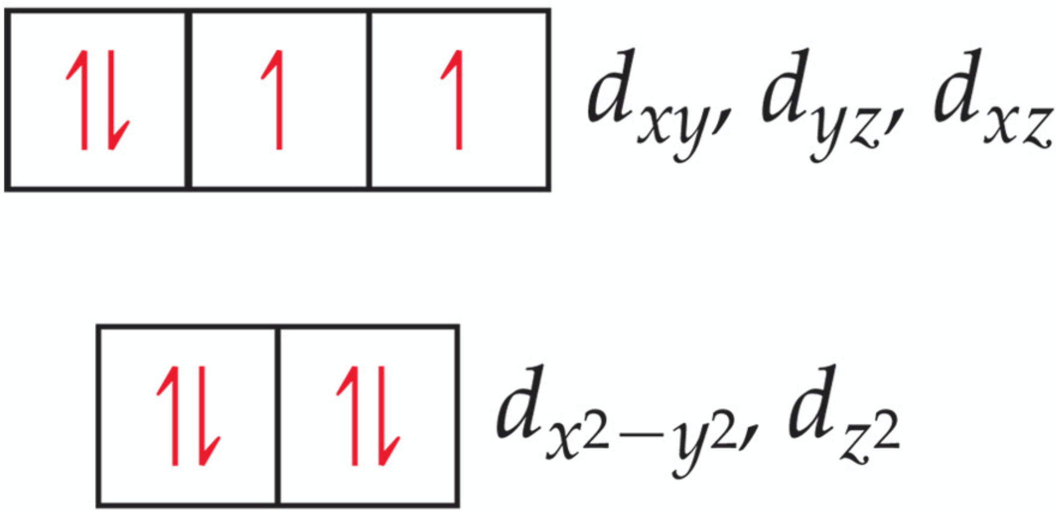
Increasing Δ

$Cl^- < F^- < H_2O < NH_3 <$ en $< NO_2^- < CN^-$

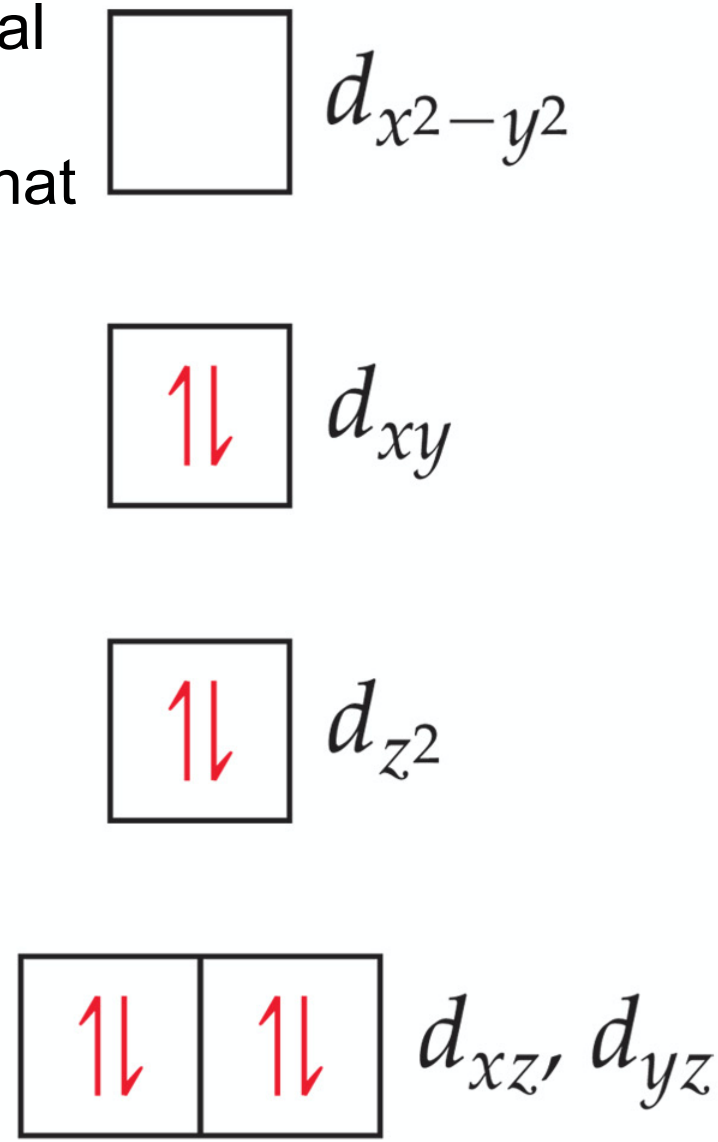


Know low spin versus high spin

There is also splitting from tetrahedral And square planar. Know they are different, don't remember exactly what square planer looks like.



Tetrahedral



Square planar

- EXAM 4
- 3 Valence Bond Theory
- 3 Molecular Orbital Theory
- 2 color of complexes
- 5 electron config/charge/oxidation state/coordination number of metal complexes
- 1 isomers
- 1 naming
- 4 Crystal Field Theory
- 1 alkane/alkene
- 1 organic isomers
- 1 naming organic molecules
- 1 organic reactions
- 2 functional groups

Exam breakdown:

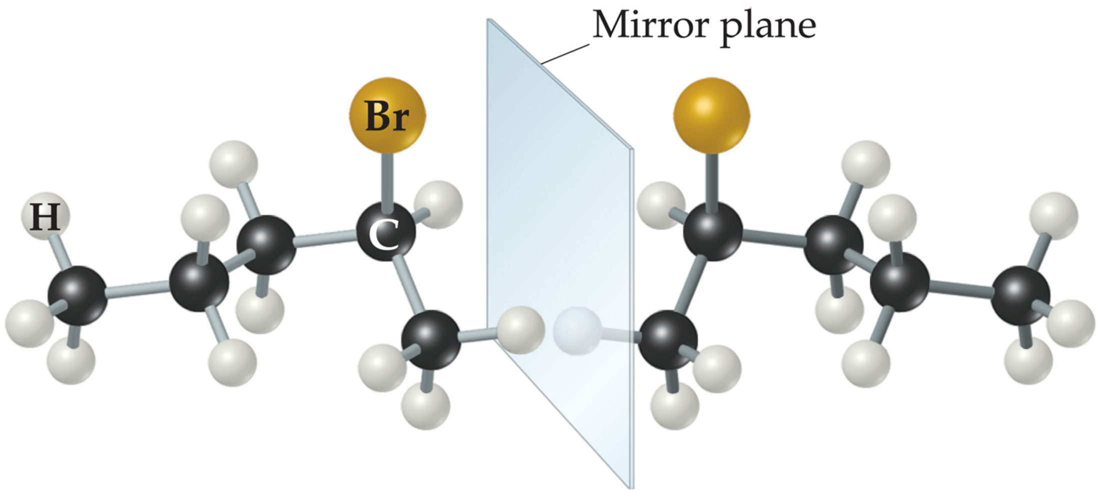
Valence bond/molecular orbital theory
Valence bond/hybridization
M.O. diagrams
Intermolecular forces

Transition metals
Color/absorption
Isomers
Electron config/magnetism/high/low spin
Ox#/coord#

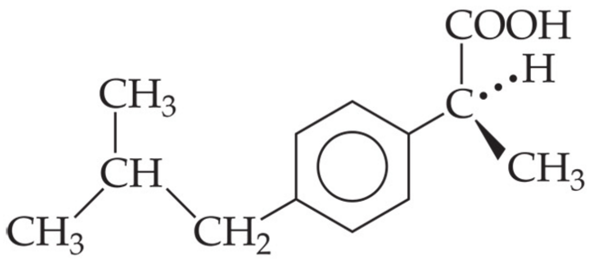
Organic
Naming org. compounds
Molecular structure/isomers

Chirality

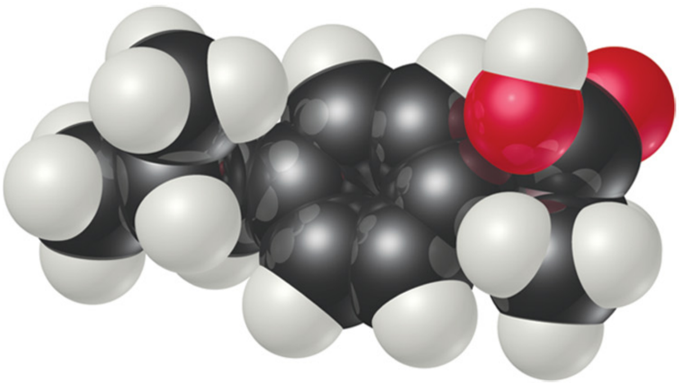
- Carbons with four different groups attached to them are handed, or chiral.
- Optical isomers or stereoisomers
- If one stereoisomer is "right-handed," its enantiomer is "left-handed."



Chirality

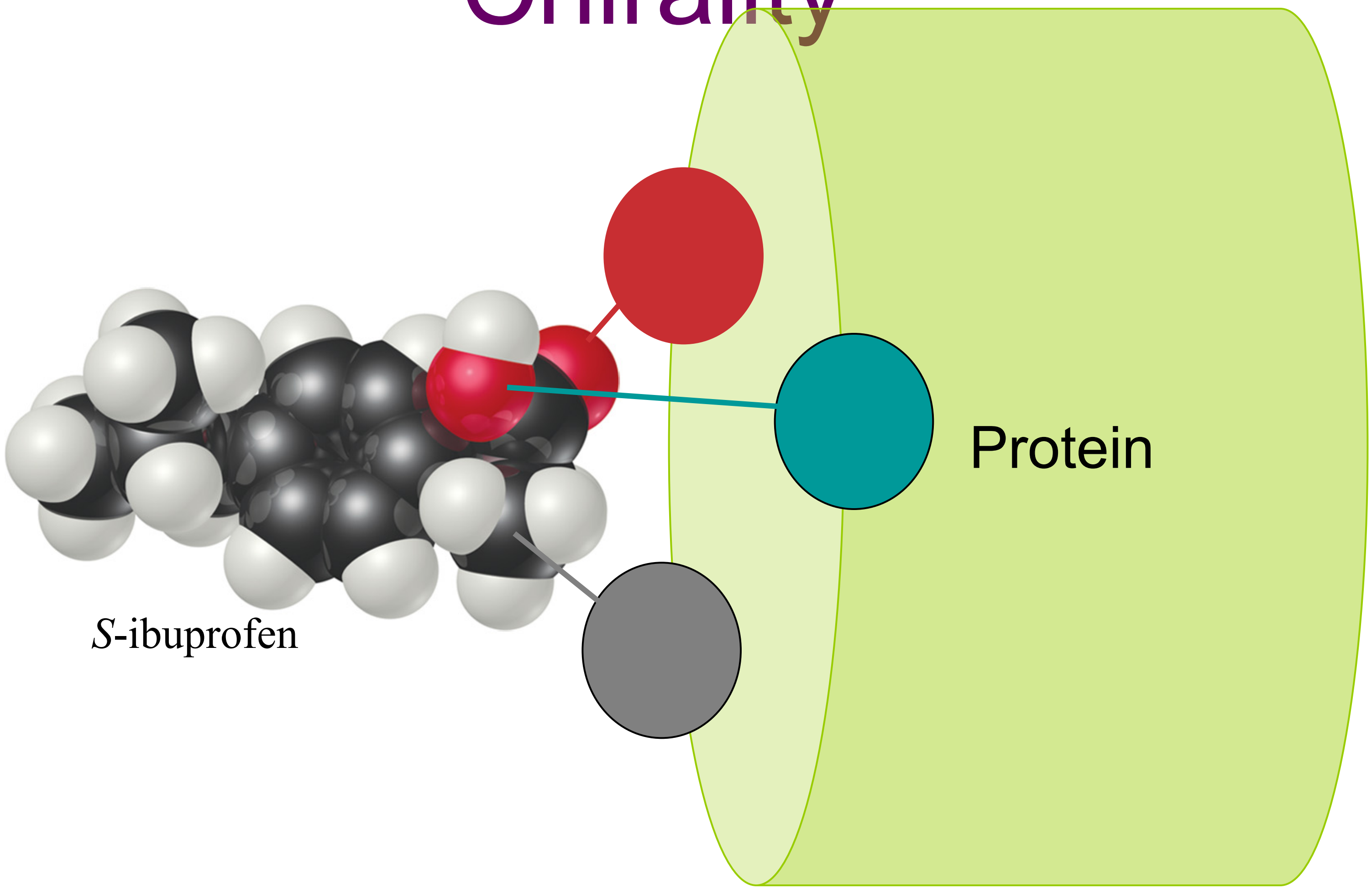


S-ibuprofen



- Many pharmaceuticals are chiral.
- Often only one enantiomer is clinically active.
- Why?

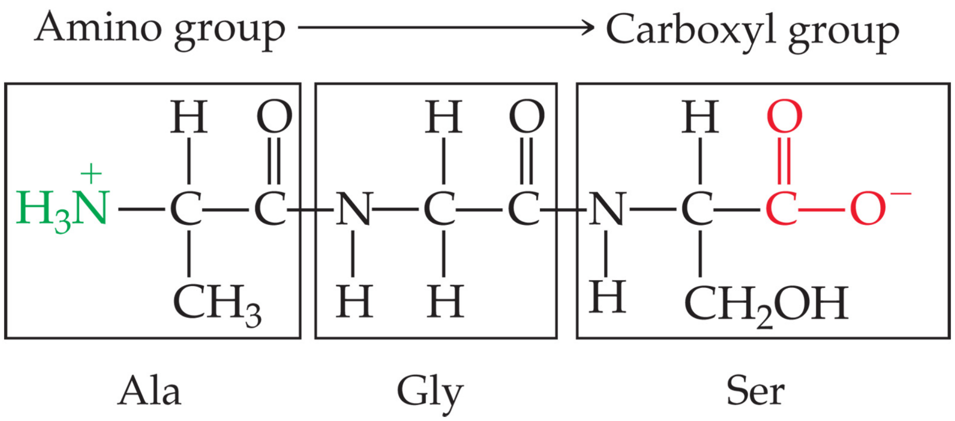
Chirality



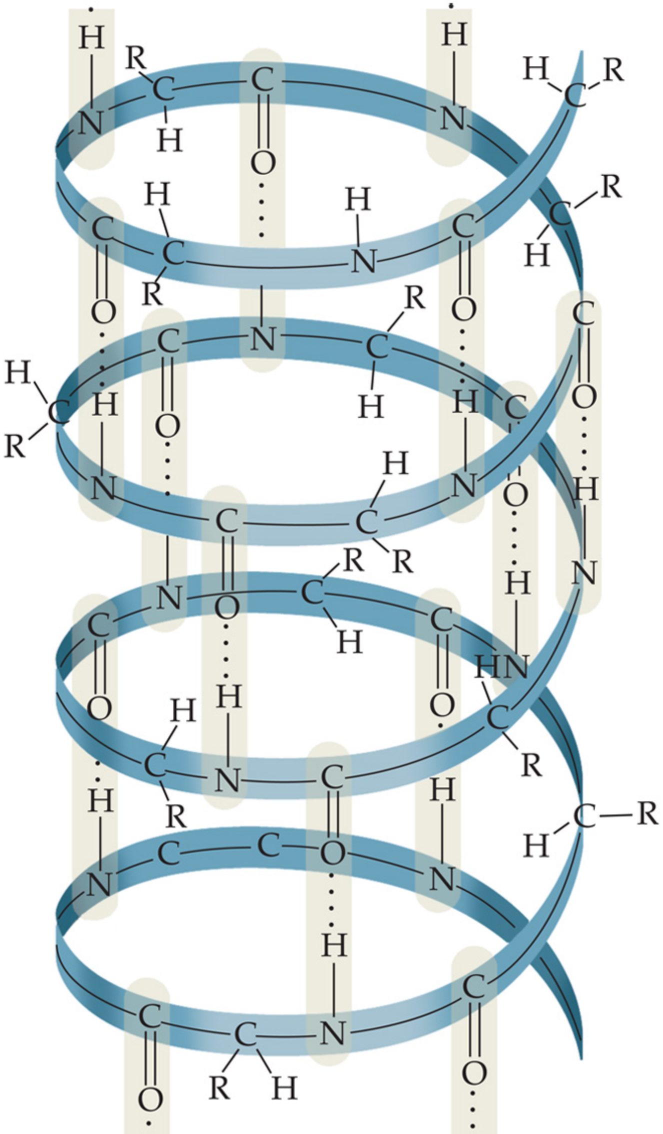
- Because they interact with a chiral protein binding site.

Amino Acids and Proteins

- Proteins are polymers of α-amino acids.
- A condensation reaction between the amine end of one amino acid and the acid end of another produces a peptide bond.

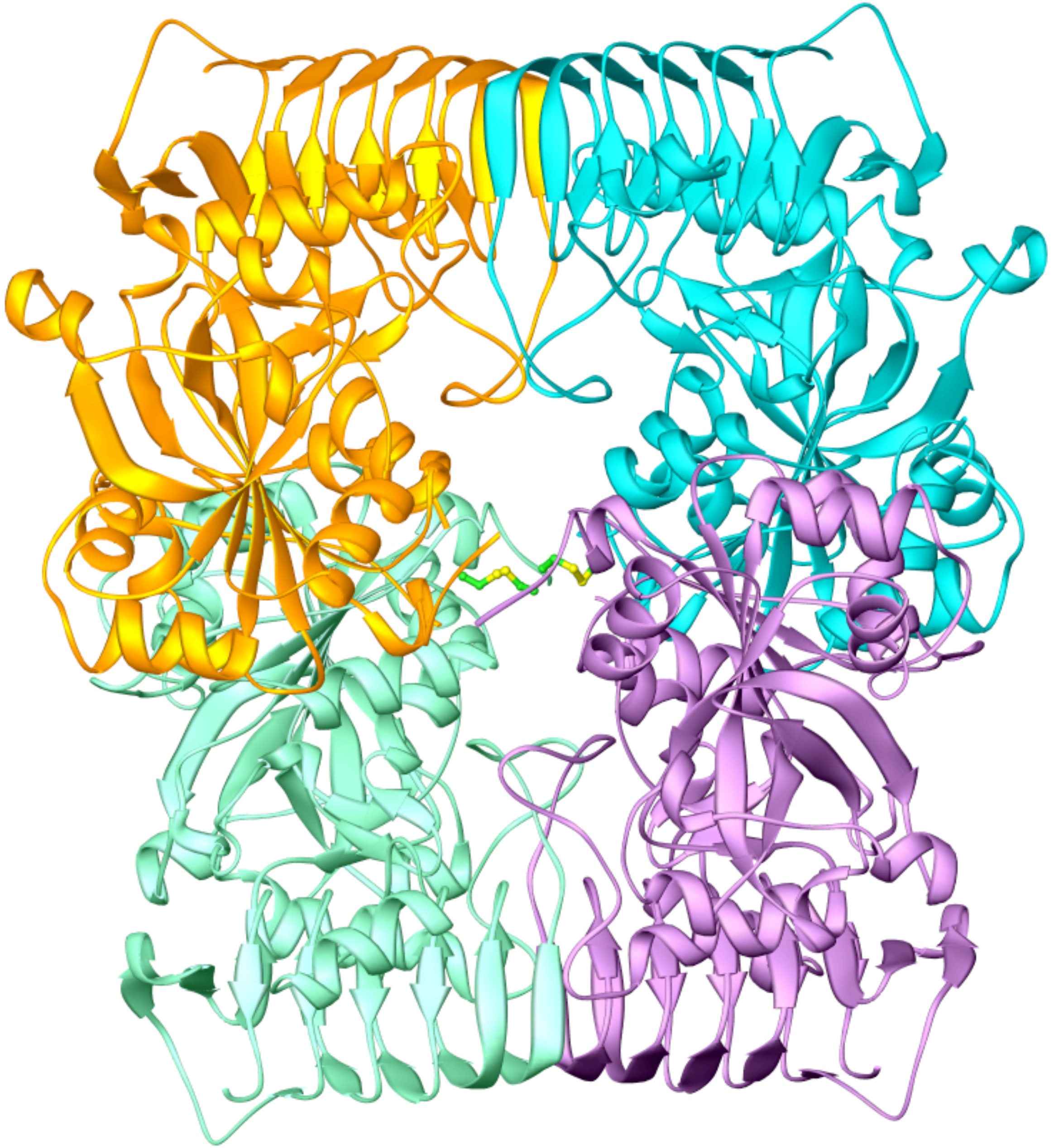


Amino Acids and Proteins



- Hydrogen bonding in peptide chains causes coils and helices in the chain.
- Kinking and folding of the coiled chain gives proteins a characteristic shape.

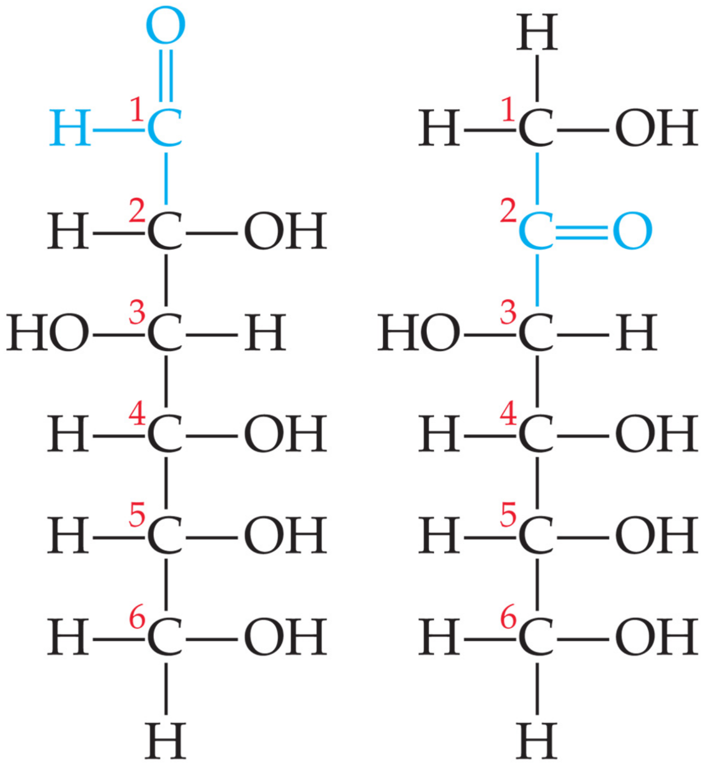
Amino Acids and Proteins



pyrophosphorylase makes starch in plants
The complete molecule is a tetramter. It's mass is 240,000 amu.

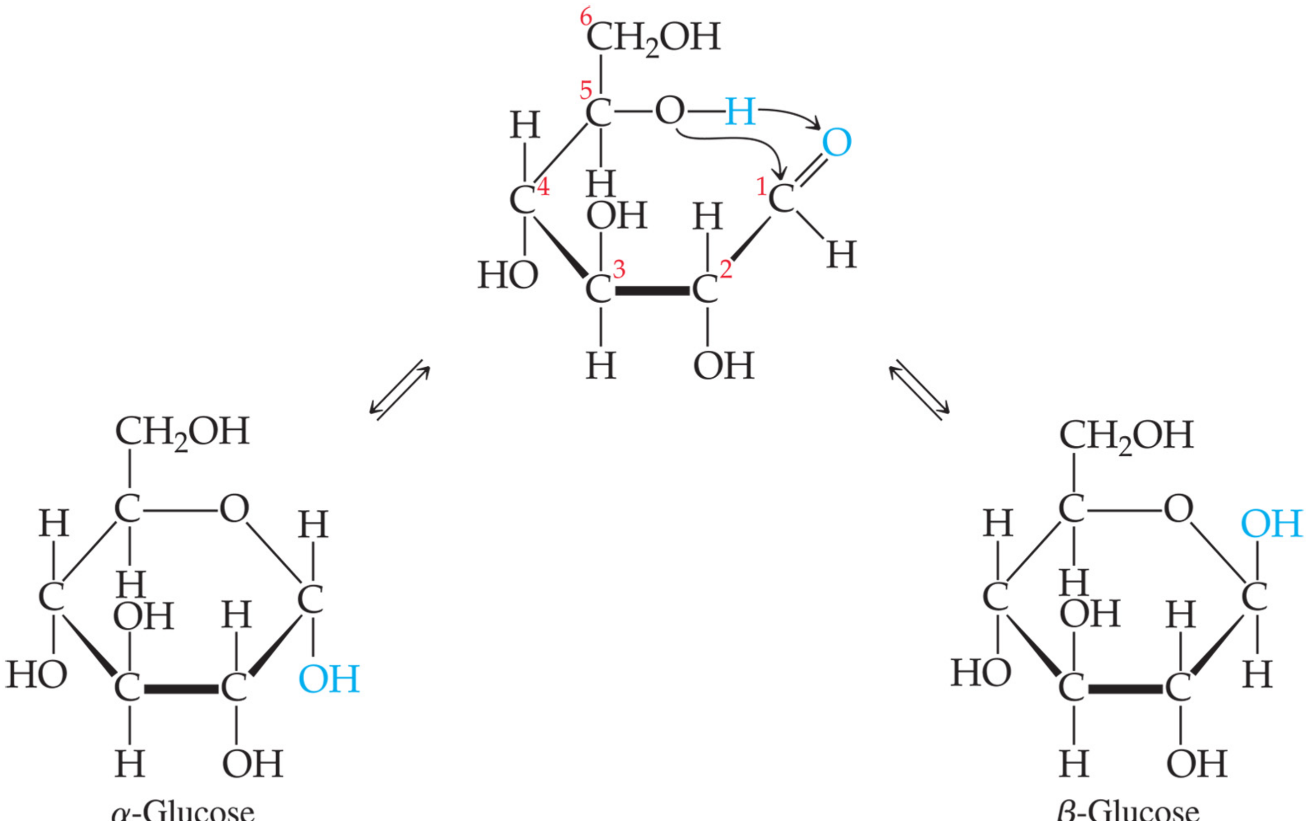
Carbohydrates

Simple sugars are polyhydroxy aldehydes or ketones.

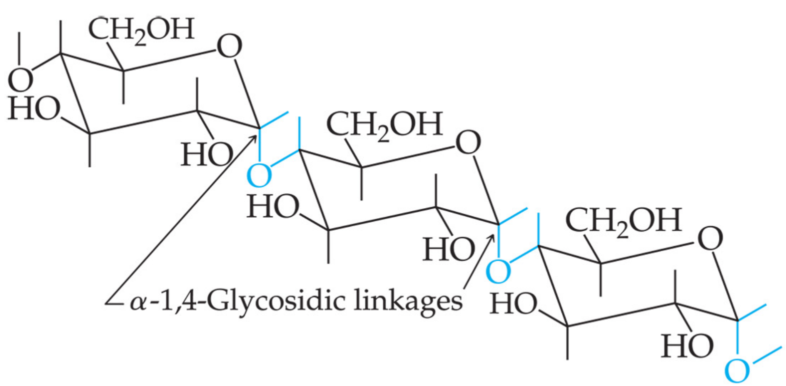


Glucose Fructose

Carbohydrates



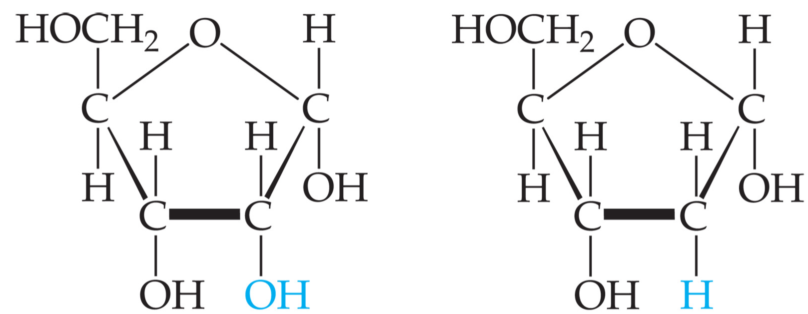
- In solution they form cyclic structures.



•These can form chains of sugars that form structural molecules such as starch and cellulose.

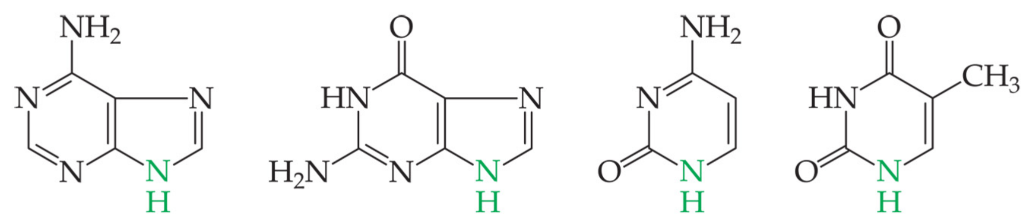
Nucleic Acids

Two of the building blocks of RNA and DNA are sugars (ribose or deoxyribose)



Ribose Deoxyribose

And cyclic bases (adenine, guanine, cytosine, and thymine or uracil).



Adenine (A) DNA RNA

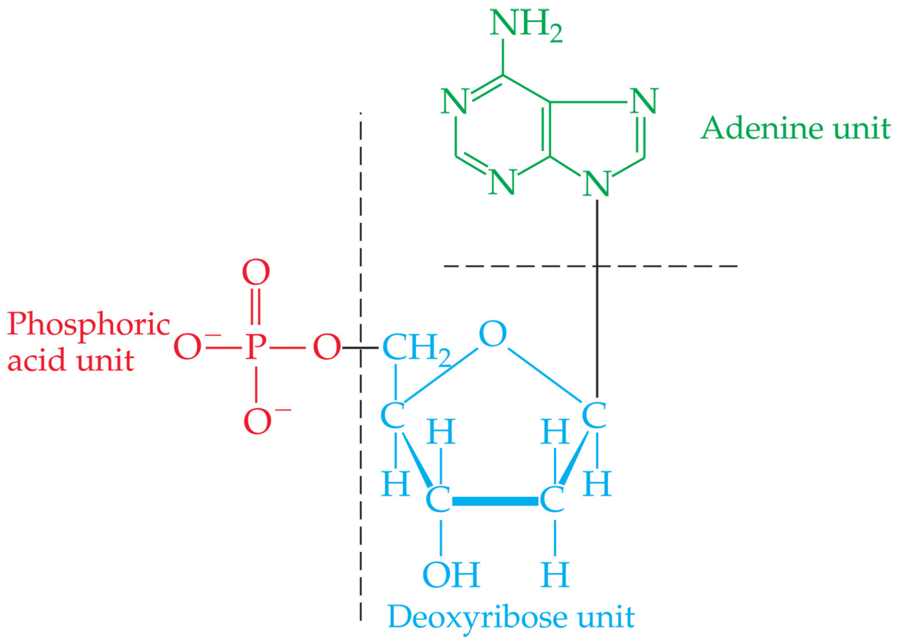
Guanine (G) DNA RNA

Cytosine (C) DNA RNA

Thymine (T) DNA

Uracil (U) RNA

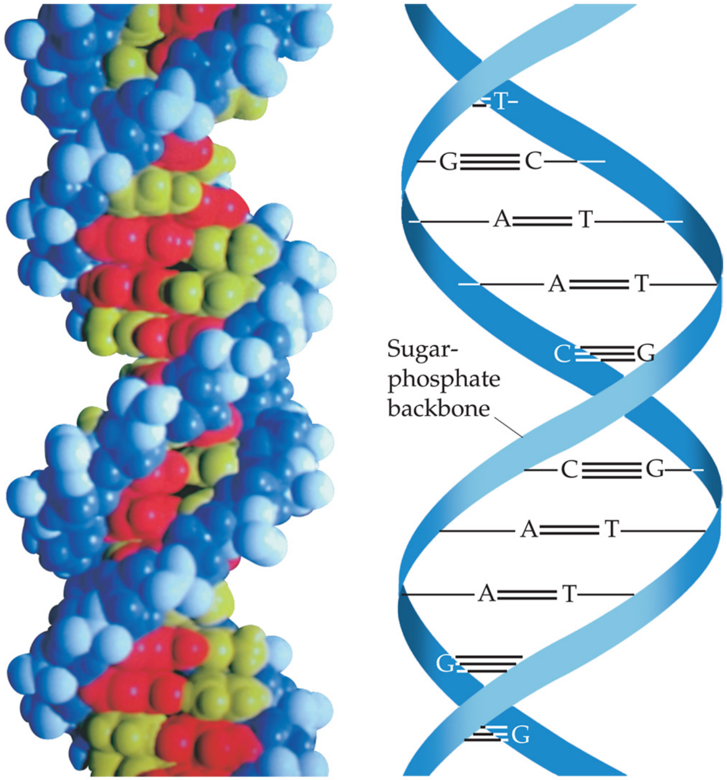
Nucleic Acids



These combine with a phosphate to form a nucleotide.

Nucleic Acids

Nucleotides combine to form the familiar double-helix form of the nucleic acids.



The FINAL

The best preparation:

1. **The four exams** and 6 quizzes.

   "I' ll bet, since I' m, after all, a little lazy, that I' ll use some of these questions"

   Topics:

   Chapter 1.
   Dimensional analysis (at least 1 problem)
   significant figures

The FINAL

Chapter 2.

History of atomic structure   (2 problems)

- dalton
- cathode ray tubes
- rutherford gold foil experiment
- Miliken's oil drop experiment
- atomic numbers, mass, isotopes
- average at. weights
- The periodic table
  - groups, periods, etc.
- molecular and empirical formulas
- ions, ionic compounds naming inorganic compounds
- naming binary molecular compounds
- (nitrogen triodide)

The FINAL

Chapter 2.
compounds
- naming binary molecular compounds
- (nitrogen triodide)
- atomic structure, protons, neutrons, electrons

Chapter 3.
- stoichiometry calculations
- dealing with chemical reactions
- limiting reagent
- calculate empirical formula

The FINAL

Chapter 4, aqueous reactions, solution stoichiometry

- strong and weak electrolytes
- the strong acids and the strong bases
- Know your anions and cations.
- precipitation reactions
- acid/base reactions
- Redox, oxidations numbers, redox reactions.
- the activity series
- solution stoichiometry
- titrations

The FINAL

Chapter 5, thermochemistry

- Kinetic and potential energy
- what is work versus heat?
- ΔH and ΔE
- what is a state function
- pV work
- calorimetry
- Hess's law
- enthalpies of formation

The FINAL

Chapter 6, electronic structure of atoms

- wave and particle nature of light
- black body radiation, quantization of energy
- photons
- The photoelectric effect
- Line spectra & the bohr model
- Quantum mechanics
  - atomic numbers
  - atomic orbitals
  - electron spin
  - electron configuration
  - The periodic table explained

The FINAL

Chapter 7, Periodic properties of the elements

- effective nuclear charge
- sizes of atoms
- sizes of ions
- ionization energies
- electron affinities
- group trends for:
- alkali metals
- alkine earch metals
- oxygen group, halogens, noble gases

The FINAL

Chapter 8, chemical bonding

- ionic bonding
- metal bonding
- covalent bonding
- bond polarity
- electronegativity
- lewis structures
- multiple bonds
- resonance structures
- octet rule and exceptions
- bond enthalpy and bond length

The FINAL

Chapter 9, VSEPR, valence bond and molecular orbital theory
self explanatory.

Chapter 25, organic and biochemistry

- hydrocarbons
- functional groups
- naming organic compounds
- isomers
- what's an amino acid?
- What's a protein?
- What's a sugar?
- polysaccharide?

The exam, the lowdown:

- questions from the previous 4 exams.
  - Exam 1:
  - Exam 2:
  - Exam 3:
  - Exam 4: