

# ORGANIC CHEMISTRY I

## (ORGANIC CHEMISTRY FUNDAMENTALS)

### FUNDAMENTALS

#### BONDING IN ORGANIC COMPOUNDS

##### Types of chemical bonds

**A. Covalent bond:** Formed when two elements share valence electrons so that both gain full valence shells. Bonds can be single (two shared electrons), double (four shared electrons), or triple (six shared electrons).

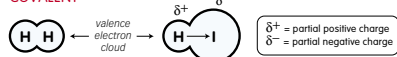
**1. Valence electrons:** Electrons in the outermost occupied electron shell of an atom.

**2. Octet Rule:** An atom is most stable when its valence shell is completely full; an atom can obtain a full valence shell by bonding with other atoms. Does not always apply to atoms with electrons in *d* orbitals.

**B. Ionic bond:** Formed when the electronegativities of the bonded atoms are significantly different. Both shared electrons are almost completely associated with the more electronegative atom, which becomes an anion (negatively charged) while the other atom becomes a cation (positively charged).

##### Covalent and ionic bonding

##### COVALENT

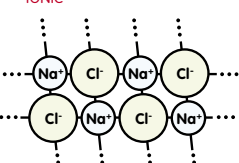


**Nonpolar:** Bonded H atoms share valence electrons equally

**Polar:** Bonded H and I atoms share electrons unequally

$\delta^+$  = partial positive charge  
 $\delta^-$  = partial negative charge

##### IONIC



Oppositely charged ions bond to each other to form **lattice structures**.

##### METALLIC



Metal nuclei are held together by a delocalized "sea" of electrons

##### Bond characteristics

**A. Bond order:** Half the number of electrons shared in a covalent bond. The higher the bond order, the stronger and shorter the bond compared to a lower order bond between the same two atoms; e.g., a C=C bond (bond order of 2) is stronger and shorter than a C-C bond (bond order of 1).

**B. Bond polarity:** In bonds between atoms of unequal electronegativities, shared electrons are more likely to be found near the more electronegative atom. Such a bond is said to be *polar*.

- Electronegativity:** Ability of an atom in a molecule to attract electrons. Increases traveling across a period from left to right in the Periodic Table of the Elements, and decreases traveling down a group in the Periodic Table.

**C. Bond strength:** Energy required to break a chemical bond. The higher the energy, the stronger the bond.

#### GEOMETRY OF MOLECULES

##### A. Valence shell electron pair repulsion (VSEPR) theory:

Model for predicting molecular geometry. Based on the idea that, in a molecule, electron pairs arrange themselves as far apart as possible to minimize electron-electron repulsion.

- The shape of a molecule is determined by the number of electron pairs (bonding pairs and lone pairs) associated with the central atom of the molecule.

**B. Valence bond theory:** Theory of bonding that states that covalent bonds form through the spatial overlap of orbitals containing valence electrons. Valence bond theory is consistent with the geometric predictions of VSEPR theory.

**1. Hybridization:** Formation of hybrid orbitals, which are mixtures of individual atomic orbitals.

- The number of atomic orbitals used to create a set of hybrid orbitals equals the number of orbitals generated by hybridization.
- Hybrid orbitals can hold up to two electrons; half-filled hybrid orbitals can share electrons with other half-filled orbitals to form a covalent bond.

**2. Sigma ( $\sigma$ ) bonds:** Bonds formed by the head-on overlap of *sp*, *sp*<sup>2</sup>, or *sp*<sup>3</sup> hybrid orbitals with each other or with hydrogen 1s orbitals.

**3. Pi ( $\pi$ ) bonds:** Bonds formed by the sideways overlap of *p* orbitals.

**4. Pi ( $\pi$ ) electrons:** Electrons in a  $\pi$  orbital (either bonding or nonbonding).

#### Hybrid orbitals and their corresponding VSEPR geometries

Atomic orbitals combined	Hybrid orbitals formed	Bonding electron pairs and lone pairs around central atom	VSEPR geometry
1s orbital & 1p orbital	sp hybrid (2 orbitals)	2	linear
1s orbital & 2p orbitals	sp <sup>2</sup> hybrid (3 orbitals)	3	trigonal planar
1s orbital & 3p orbitals	sp <sup>3</sup> hybrid (4 orbitals)	4	tetrahedral
1s orbital & 3p orbitals & 1d orbital	dsp <sup>3</sup> hybrid (5 orbitals)	5	trigonal bipyramidal
1s orbital & 3p orbitals & 2d orbitals	d <sup>2</sup> sp <sup>3</sup> hybrid (6 orbitals)	6	octahedral

#### DRAWING ORGANIC MOLECULES

**A. Lewis structure:** A molecular representation that depicts covalent bonds and nonbonding valence electrons.

**1. Resonance structures:** Some Lewis structures have multiple, distinct, but equivalent ways of arranging multiple bonds and electrons, while still obeying the Octet Rule and maintaining the connectivity of atoms in the molecule. Each equivalent arrangement is called a *resonance structure*.

- In reality, molecules exist as the average of all their different resonance structures. Individual resonance structures cannot be isolated because electrons in a molecule are actually delocalized and multiple bond characteristics can be spread out over the entire molecule.

**2. Formal charge:** The formal charge on an atom equals the number of valence electrons in the unbonded atom minus both the number of lone-pair electrons the atom has and the number of covalent bonds to the atom.

- A nonzero formal charge indicates that an atom has a different number of valence electrons than it would if it were unbonded and neutral.

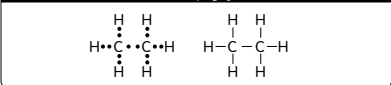
- The sum of the individual formal charges in a molecule equals the overall charge of the molecule; formal charges give a sense of where charge is localized within a molecule.

##### CARBON MONOXIDE, CO

	Carbon	Oxygen
$\text{C} \equiv \text{O} :$	4 valence electrons	6 valence electrons
Unbonded	4 valence electrons	6 valence electrons
In CO molecule	2 lone-pair electrons 3 covalent bonds	2 lone-pair electrons 3 covalent bonds
Formal charge	4 - 2 - 3 = -1	6 - 2 - 3 = +1

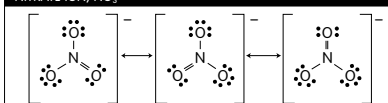
Formal charges on the atoms in carbon monoxide. The net charge on the molecule is  $-1 + 1 = 0$ .

##### ETHANE, C<sub>2</sub>H<sub>6</sub>

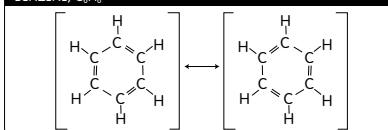


Lewis structure. Dots represent electrons and lines represent covalent bonds.

##### NITRATE ION, NO<sub>3</sub><sup>-</sup>



##### BENZENE, C<sub>6</sub>H<sub>6</sub>



Resonance structures of nitrate ion and benzene. The actual molecules are an average of their individual resonance structures.

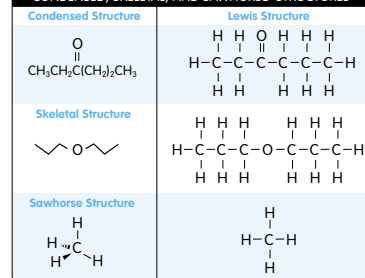
**B. Condensed structure:** Short-hand method of representing organic molecules in which some or all bonds are not explicitly drawn.

**C. Skeletal structure:** Representation of an organic molecule in which:

- carbon atoms and hydrogen atoms bonded to carbon are not explicitly drawn.
- carbon-carbon bonds are represented by lines, with carbon atoms assumed to be present at the intersection of any two lines and at the ends of lines.
- any carbon not explicitly making four covalent bonds is implicitly bonded to however many hydrogen atoms are necessary to give that carbon four bonds.

**D. Sawhorse structure:** Shows the three-dimensional arrangement of atoms in a molecule. Dotted wedges indicate bonds pointing into the plane of the paper; solid wedges indicate bonds rising from the plane of the paper; and solid lines indicate bonds that are in the plane of the paper.

#### CONDENSED, SKELETAL, AND SAWHORSE STRUCTURES



#### COMMON ATOMS IN ORGANIC CHEMISTRY

##### A. Carbon

- Forms four bonds to fulfill Octet Rule.
- Orbital hybridization in carbon:**
  - sp<sup>3</sup>-hybridized carbon:** Carbon atoms that are single-bonded to four separate atoms form their bonds through *sp*<sup>3</sup>-hybrid orbitals; atoms on an *sp*<sup>3</sup>-hybridized carbon atom have tetrahedral geometry.
  - sp<sup>2</sup>-hybridized carbon:** Carbon atoms that are double-bonded to one atom and single-bonded to two others form their  $\sigma$  bonds through *sp*<sup>2</sup>-hybrid orbitals; the double-bonded atom is linked to the carbon atom by one of these  $\sigma$  bonds plus a  $\pi$  bond between the carbon atom's remaining *p* orbital and a *p* orbital from the atom; atoms on an *sp*<sup>2</sup>-hybridized carbon atom have trigonal planar geometry.
  - sp-hybridized carbon:** Carbon atoms that are triple-bonded to one atom and single-bonded to one other form their  $\sigma$  bonds through *sp*-hybrid orbitals; the triple-bonded atom is linked to the carbon atom by one of these  $\sigma$  bonds plus two  $\pi$  bonds between the carbon atom's two remaining *p* orbitals and two *p* orbitals from the atom; the atoms on an *sp*-hybridized carbon have linear geometry.

##### B. Hydrogen

- Forms one bond to fulfill Octet Rule.
- Has one electron in its 1s orbital; can only form  $\sigma$  bonds; does so through head-on overlap of its 1s orbital with orbitals from other atoms.

##### C. Nitrogen

- Usually forms three bonds to fulfill Octet Rule and has one lone-pair of electrons.
- Can also use its lone pair to form four bonds (and gain a positive formal charge), or gain a lone pair and form two bonds (and gain a negative formal charge).

## FUNDAMENTALS (CONTINUED)

- **Orbital hybridization in nitrogen:** Nitrogen atoms making only single bonds to other atoms do so through  $sp^3$ -hybrid orbitals; when nitrogen makes three single bonds, one of its four hybrid orbitals contains a lone pair of electrons and does not participate in bonding, inducing a pyramidal geometry in the nitrogen atoms.

### D. Oxygen

- Usually forms two bonds to fulfill Octet Rule and has two electron lone pairs; can also use a lone pair to form three bonds (and gain a positive formal charge) or gain a lone pair and form one bond (and gain a negative formal charge).

### • Orbital hybridization in oxygen:

- Oxygen atoms making only single bonds to other atoms do so through  $sp^3$  hybrid orbitals; when oxygen makes two single bonds, two of its hybrid orbitals each contain a lone pair of electrons and do not participate in bonding, inducing a bent geometry in the oxygen atoms.

### E. Halogens (Fluorine, Chlorine, Iodine, etc.)

- Usually form one bond to fulfill Octet Rule and have three lone-pairs of electrons.

### • Orbital hybridization in halogens:

- Halogens form single bonds in organic compounds through an  $sp^3$  hybrid orbital; the other three of these four hybrid orbitals each contain a lone pair of electrons and do not participate in bonding.

### F. Boron

- Boron atoms that are single-bonded to three separate substituents form their bonds through  $sp^2$  hybrid orbitals.
- The remaining  $p$  orbital on boron remains empty and makes trivalent boron (i.e., a boron atom that has three substituents) a Lewis acid, as the empty  $p$  orbital can accept an electron lone pair.

### G. Phosphorus

- Somewhat common in organic chemistry.
- Trivalent phosphorus is similar to nitrogen.
- Can form up to six covalent bonds because of its empty, relatively low-energy  $d$  orbitals.

### H. Sulfur

- Somewhat common in organic chemistry.
- Divalent sulfur (i.e., a sulfur atom that has two substituents) is similar to oxygen.
- Can form up to six covalent bonds because of its empty, relatively low-energy  $d$  orbitals.

## TYPES OF ORGANIC MOLECULES AND FUNCTIONAL GROUPS

**Hydrocarbons:** molecules that contain only carbon and hydrogen

- A. **Aliphatic hydrocarbons:** Do not contain a benzene ring or any other aromatic system.

1. **Alkanes:** Aliphatic hydrocarbons that contain only single bonds and do not contain rings of bonded atoms; also called saturated hydrocarbons.

- General formula  $C_nH_{2n+2}$ , where  $n$  is an integer.

2. **Alkenes:** Unsaturated hydrocarbons containing one or more carbon-carbon double bonds.

- General formula  $C_nH_{2n+2-2d}$ , where  $d$  = # of double bonds in the molecule and  $n$  is an integer.

3. **Alkynes:** Unsaturated hydrocarbons containing one or more carbon-carbon triple bonds.

- General formula  $C_nH_{2n+2-4t}$ , where  $t$  = # of triple bonds in the molecule and  $n$  is an integer.

4. **Cycloalkanes:** Unsaturated hydrocarbons containing one or more rings of bonded carbon atoms.

- General formula  $C_nH_{2n+2-2r}$ , where  $r$  = # of rings in the molecule and  $n$  is an integer.
- Tend not to be flat because of the tetrahedral bond-angle requirements of carbon.
- Cyclopentane ( $C_5H_{10}$ ) and cyclohexane ( $C_6H_{12}$ ) are the most stable cycloalkanes; other cycloalkanes have more ring strain (i.e., destabilization of a ring due to the bond angles of atoms in a ring deviating from the  $109.5^\circ$  preferred by  $sp^3$ -hybridized carbons).

- B. **Conjugated hydrocarbons:** Hydrocarbons containing a series of three or more overlapping  $p$  orbitals (e.g., a series of alternating double and single bonds); conjugation contributes to the stability of a molecule, due to the delocalization of  $\pi$  electrons over the length of the conjugated system.

- C. **Aromatic hydrocarbons:** Special type of conjugated molecule containing a benzene ring or some other aromatic system; unusually stable because of their unique electronic configuration and delocalization of  $\pi$  electrons.

1. **Benzene:**  $C_6H_6$ ; the parent compound of the aromatic hydrocarbon family.

2. **Arenes:** Benzene derivatives in which one or more hydrogen atoms from benzene are replaced by other functional groups.

3. **Huckel's Rule:** A molecule is aromatic if it contains a planar, cyclic, conjugated system possessing  $4n + 2$  (where  $n$  is an integer)  $\pi$  electrons.

### Functional groups:

Atoms or groups of bonded atoms that bond to carbon atoms to give rise to other families of organic compounds. A given functional group will generally undergo the same type of reactions regardless of the molecule in which it appears. When a functional group is bonded to an atom, it is called a *substituent* of that atom.

### Degree of alkyl substitution:

Number of alkyl group substituents on a given atom (usually carbon). An atom that has alkyl substituents can be *primary* (one alkyl substituent), *secondary* (two alkyl substituents), *tertiary* (three alkyl substituents), or *quaternary* (four alkyl substituents).

### Common organic functional groups

FUNCTIONAL GROUP	STRUCTURE
ALKYL (R-)	Composed only of single bonded carbons and hydrogens
ALKOXY	$R-\ddot{O}-$
HYDROXYL	$H-\ddot{O}-$
AMINO	$\begin{array}{c} H & R & R_2 \\   &   &   \\ :N- & - & - \\   &   &   \\ H & H & R_1 \end{array}$ or $\begin{array}{c} R \\   \\ :N- \\   \\ H \end{array}$ or $\begin{array}{c} R_2 \\   \\ :N- \\   \\ R_1 \end{array}$
HALO	$:\ddot{X}-$ (X = F, Cl, Br, I)
CARBONYL	$\begin{array}{c} O \\    \\ C \\   \end{array}$
PHENYL (Ph-)	
BENZYL (Bz-)	

### Classes of molecules:

- A. **Alcohols:** Molecules containing one or more hydroxyl groups bonded to alkyl groups.

- B. **Alkyl halides:** Molecules containing one or more halogen atoms bonded to alkyl groups.

- C. **Amines:** Molecules containing one or more amino groups bonded to alkyl groups.

- D. **Ethers:** Molecules containing two alkyl groups bonded to the same oxygen atom.

1. **Epoxides:** Ethers containing an oxygen atom bonded to two other carbon atoms in a three-membered ring.

- E. **Carbonyls:** Molecules containing one or more carbonyl groups.

1. **Aldehydes:** Molecules containing a carbonyl group bonded to a hydrogen atom and an alkyl group.

2. **Ketones:** Molecules containing a carbonyl group bonded to two alkyl groups.

3. **Carboxylic acids:** Molecules containing a carbonyl group bonded to a hydroxyl group and an alkyl group.

4. **Esters:** Molecules containing a carbonyl group bonded to an alkoxy group and an alkyl group.

5. **Acid chlorides:** Molecules containing a carbonyl group bonded to a chloride group and an alkyl group.

6. **Amides:** Molecules containing a carbonyl group bonded to an amino group and an alkyl group.

### Common classes of organic molecules

TYPE OF MOLECULE	STRUCTURE
ALKANE	Composed only of single bonded carbons and hydrogens
ALKENE	
ALKYNE	
ALCOHOL	$R-\ddot{O}-H$
ALKYL HALIDE	$R-\ddot{X}$
AMINE	$\begin{array}{c} R \\   \\ :N-H \\   \\ H \end{array}$ or $\begin{array}{c} R_1 \\   \\ :N-R_2 \\   \\ H \end{array}$ or $\begin{array}{c} R_1 \\   \\ :N-R_2 \\   \\ R_3 \end{array}$
ETHER	$R_1-\ddot{O}-R_2$
EPOXIDE	
ALDEHYDE	$\begin{array}{c} :O \\    \\ R-C-H \end{array}$
KETONE	$\begin{array}{c} :O \\    \\ R_1-C-R_2 \end{array}$
CARBOXYLIC ACID	$\begin{array}{c} :O \\    \\ R-C-\ddot{O}-H \end{array}$
ESTER	$\begin{array}{c} :O \\    \\ R_1-C-\ddot{O}-R_2 \end{array}$
ACID CHLORIDE	$\begin{array}{c} :O \\    \\ R-C-Cl \end{array}$
AMIDE	$\begin{array}{c} :O \\    \\ R-C-\ddot{N}-H \\   \\ H \end{array}$

**IUPAC rules:** A system set forth by the International Union of Pure and Applied Chemistry (IUPAC) for naming organic molecules.

### A. IUPAC rules for alkane molecules

1. Count the number of carbon atoms in the longest continuous carbon chain in the molecule. Based on the number of carbon atoms in the chain, write its name as if it were a simple straight-chain alkane. This name is the base of the name of the whole molecule.

- If the molecule contains multiple chains of equal length, the parent chain is the one that has the most branch-off points.

Carbons	Alkane name	Carbons	Alkane name
1	Methane	7	Heptane
2	Ethane	8	Octane
3	Propane	9	Nonane
4	Butane	10	Decane
5	Pentane	11	Undecane
6	Hexane	12	Dodecane

2. Number each carbon atom in the parent chain, starting from the end of the chain closer to its nearest branch-off point. If both ends of the chain are the same distance from their nearest branch-off points, start from the end closer to its second-nearest branch-off point.

3. Consider every branch-off of the parent chain to be a separate hydrocarbon. Name each branch based on its length, but replace the ending "-ane" with "-yl." For each branch, note the number (from Step 2) of the carbon atom on the parent chain to which it is attached and precede the branch name with this number. If there are two or more identical branches off of the main chain, separate the numbers of the carbons to which the identical substituents are attached with commas, and precede the name of the branch with the appropriate numerical prefix (di-, tri-, etc.).

CONTINUED ON OTHER SIDE

## FUNDAMENTALS (CONTINUED)

4. Write out the name of the molecule by adding the branch names from Step 3 (in alphabetical order, ignoring the branch numbers and numerical prefixes) to the name of the parent chain from Step 1.

**NAMING AN ALKANE MOLECULE**

**STEP 1**

Parent compound is **heptane**.

**STEP 2**

**STEPS 3 & 4**

Branches are **3-methyl** and **5-ethyl**.  
Compound is **5-ethyl-3-methylheptane**.

### B. IUPAC rules for molecules containing other functional groups:

- Alkenes:** Follow the rules for naming alkanes, but choose the longest carbon chain containing the double bond as the parent chain in Step 1, and begin numbering the parent chain with the carbon closest to the double bond in Step 2. Change the ending of the parent chain name from "-ane" to "-ene," and indicate the position of the double bond by preceding the name of the parent chain with the number of the first carbon involved in the double bond.
- Alkynes:** Follow the rules for naming alkenes, changing the ending of the parent chain name from "-ene" to "-yne."
- Alkyl halides:** Follow the rules for naming alkanes, and name halogen substituents as if they were branches off of the main carbon chain; when naming halogen substituents, change the ending "-ine" to "-o."
- Alcohols:** Follow the rules for naming alkenes, changing the ending of the parent chain name from "-ene" to "-anol."
- Amines:** For primary amines ( $\text{RNH}_2$ ), name the alkyl substituent as if it were a branch on an alkane parent chain, and attach the suffix "-amine." For secondary and tertiary amines, choose the largest alkyl substituent on the nitrogen atom as the parent chain and change its ending from "-ane" to "-ylamine," and then name the other alkyl groups as substituents on the main chain at the "N" position.
- Ethers:** Name each substituent attached to oxygen separately. Attach them in alphabetical order to the word "ether."
- Aldehydes:** Follow the rules for naming alkanes, but in Step 1 choose the longest carbon chain containing the aldehyde group as the parent chain, and change the ending of the parent chain name from "-ane" to "-anal."
- Ketones:** Follow the rules for naming alkanes, but choose the longest carbon chain containing the carbonyl carbon as the parent chain in Step 1, and begin numbering the parent chain with the carbon closest to the carbonyl carbon.

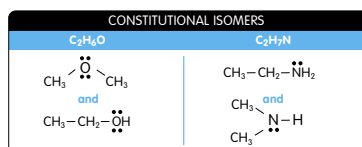
Change the ending of the parent chain name from "-ane" to "X-one," where "X" is the number of the carbonyl carbon.

- Carboxylic acids:** Follow the rules for naming alkanes, but choose the longest carbon chain containing the carboxylic acid group as the parent chain in Step 1, begin numbering from the carbonyl carbon in Step 2, and change the ending of the parent chain name from "-ane" to "-oic acid."
- Acid Chlorides, Amides, and Esters:** Follow the rules for naming carboxylic acids, but change the ending "-ic acid" to "-yl chloride" (acid chlorides), "-amide" (amides), or "-ate" (esters).

## ISOMERISM AND STEREOCHEMISTRY

**A. Isomers:** Molecules that have the same chemical formula, but are structurally different in some way.

- Constitutional isomers:** Isomers that have atoms connected to each other in different ways.

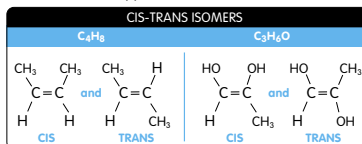


- Stereoisomers:** Isomers whose atoms have the same connectivity, but are arranged differently in space relative to each other.

**B. Geometrical isomers:** Stereoisomers whose substituents are arranged differently relative to each other around a double bond or ring.

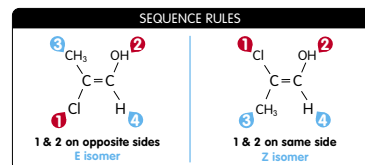
- Cis-trans isomers:** Geometrical isomers in which two identical substituents (or two pairs of two identical substituents) are bonded differently to carbon atoms participating in a double bond or ring.

- Cis isomer:** Isomer in which the identical substituents are on the same side of the double bond or ring.
- Trans isomer:** Isomer in which the identical substituents are on opposite sides of the double bond or ring.



- Sequence Rules:** Method for specifying the arrangement of substituents around a carbon-carbon double bond or a carbon-carbon bond in a ring.

- Rank the four substituents in order of the atomic numbers of the atoms bonded directly to the double bonded carbons, from highest (1) to lowest (4).
- If two substituents have the same ranking after Step 1, look at the next atoms in their substituent chains. For both substituents, list the atoms that are two bonds away from the chiral center in order of atomic number, from highest to lowest. Assign the lower number to the substituent that has the atom with the higher atomic number in the first position in its list; if this is the same for both substituents, continue down the list until a difference is found and assign a ranking in the same manner.
- If a substituent has a double (or triple) bond in its chain, it is counted as two (or three) bonds to the same atom for the purposes of making lists in Step 2.
- If multiple substituents are still the same after Step 2, move along the substituent chains until the first point of difference is found, and then rank the substituents as in Step 2.
- If the higher-priority substituents ('1' and '2') are on the same side of the double bond, then the substituents are arranged in *Z* configuration; if the higher-priority substituents are on opposite sides of the double bond, then they are arranged in *E* configuration.



Specifying the stereochemistry of isomers of  $\text{C}_3\text{H}_5\text{OCl}$

**C. Optical isomers:** Stereoisomers that have all their atoms or groups arranged in the same way relative to each other, but cannot be superimposed over each other. Optical isomers are chiral molecules.

- Chirality:** inability of a molecule to be superimposed on its mirror image so that all its atoms are in the same positions as the atoms in the mirror image. A molecule that does not have chirality is therefore achiral.

- Chiral center:** Carbon atom bonded to four different substituents. Chiral molecules usually contain chiral centers, but the presence of a chiral center does not necessarily make a molecule chiral.

- Enantiomers:** Optical isomers that are mirror images of each other.

- Diastereomers:** Optical isomers that are not mirror images of each other.

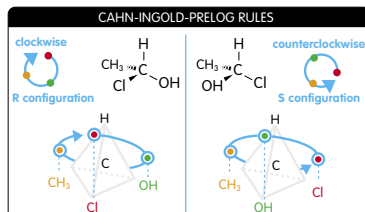
- Determining chirality:** A molecule is chiral only if it does not have a plane of symmetry (i.e., if no plane exists that can divide that molecule into two identical halves).

- Cahn-Ingold-Prelog rules:** Method for specifying the arrangement of four different substituents around a chiral center.

- Steps 1-4 are the same as Steps 1-4 of the Sequence Rules (see above).

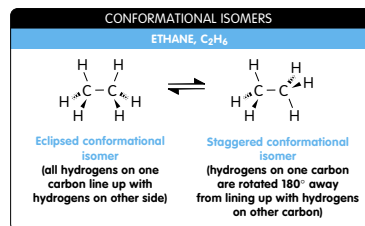
- Draw the chiral center so that the bond to the substituent ranked '4' points into the plane of the paper; the three remaining substituents will be pointing out of the plane of the paper.

- Draw a curved arrow from the substituent ranked '1' to the substituent ranked '2' to the substituent ranked '3'. If this arrow is clockwise, the chiral center has *R* configuration; if it is counterclockwise, the chiral center has *S* configuration.



Use of Cahn-Ingold-Prelog rules to specify the stereochemistry of optical isomers of  $\text{C}_2\text{H}_5\text{OCl}$

- Conformational isomers:** Stereoisomers that can be interconverted by the rotation of atoms about a  $\sigma$ -bond.



## SPECTROSCOPY OF ORGANIC MOLECULES

### BACKGROUND

**A. Spectroscopy:** Interaction of electromagnetic (EM) radiation with matter. Because the response of a compound to EM radiation depends on its structure, spectroscopy can be used to deduce the structures of unknown chemical compounds.

**B. Dual nature of EM radiation:** EM radiation behaves both as a particle of light (called a photon) and as a wave moving at the speed of light ( $c$ ;  $c = 3 \times 10^8$  m/s).

**C. Properties of EM particles and waves:**

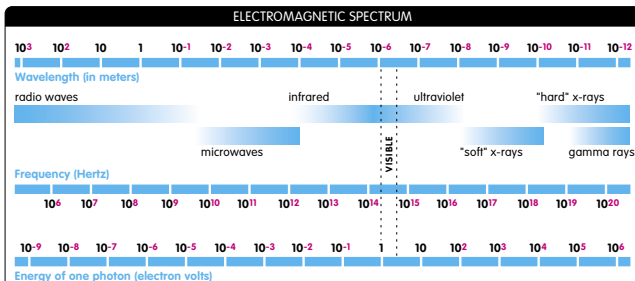
- Wavelength ( $\lambda$ ):** Distance between two peaks or troughs in a light wave.
- Frequency ( $\nu$ ):** Number of wave cycles that pass a given point per line. Usually measured in Hertz (Hz; 1 Hz = 1 cycle/second).
- Energy of a photon:**  $E = h\nu = hc/\lambda$ , where  $h$  = Planck's constant =  $6.6 \times 10^{-34}$  J/sec.

### TYPES OF SPECTROSCOPY

**A. Nuclear magnetic resonance (NMR) spectroscopy:** Measures interaction of radio waves with atomic nuclei in a magnetic field.

**B. Infrared (IR) spectroscopy:** Measures absorption of infrared light by chemical bonds.

**C. Ultraviolet/Visible (UV/Vis) spectroscopy:** Measures absorption of ultraviolet or visible light by  $\pi$  bonds.





# SPECTROSCOPY OF ORGANIC MOLECULES (CONTINUED)

## NMR SPECTROSCOPY THEORY

- Atomic nuclei have a "spin" associated with them (i.e., they act as if they were spinning about an axis) due to the spin associated with their protons and neutrons.
- Because nuclei are positively charged, their spin induces a magnetic field. When a magnetic field is applied to atomic nuclei, the magnetic fields of the nuclei align themselves either parallel or antiparallel to the applied magnetic field.
- The nuclei have a slight preference for the parallel alignment, as it has a slightly lower energy, but nuclei can flip between the two possible alignments.
- When EM radiation with energy equal to the energy difference between the two alignments is applied to the nuclei, it induces them to flip from parallel to antiparallel alignment. Rapid flipping between alignments occurs. The nuclei are said to be in *resonance*, and the energy they emit when flipping from the high to the low energy state can be measured.
- The energy at which a given nucleus achieves resonance depends on its chemical surroundings.
- NMR spectra are taken by applying a magnetic field to a sample, irradiating the sample with EM radiation whose energy is varied over a given range, and measuring the energy emitted by flipping nuclei at each energy.
  - The range of radiation energies is generally chosen such that emission from only one type of nucleus (e.g.,  $^1\text{H}$ ) in a molecule is seen.
  - NMR spectroscopy does not work for nuclei that have an even number of protons and neutrons—these nuclei have no net spin.
  - NMR spectroscopy is most commonly done on  $^1\text{H}$  and  $^{13}\text{C}$ .

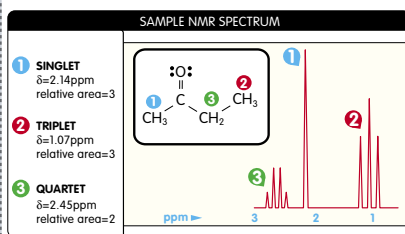
## FEATURES OF AN NMR SPECTRUM

- NMR spectra are displayed as plots of intensity of energy emission (due to resonance) versus the energy of the radiation applied to the sample. Peaks in the spectrum represent resonance energies for nuclei in a molecule.
- Shielding:** An electron cloud circulates around each nucleus and creates a small magnetic field opposing the applied magnetic field. The electron cloud around each atom depends on the surrounding atoms. As a result, each nucleus experiences a slightly different magnetic field (the sum of the applied field and the field from the electron cloud). For this reason, the energy at which a nucleus achieves resonance depends on its surroundings.
- Chemical shift ( $\delta$ ):** The resonance energy for a given nucleus is reported in an NMR spectrum as the difference (in parts/million) between the resonance frequency for a given proton and the resonance frequency for protons in a reference compound, which is usually tetramethylsilane,  $(\text{CH}_3)_4\text{Si}$ . Chemical shifts give information about the atomic surroundings of a given nucleus.
- Peak intensity:** The area under a peak in an NMR spectrum is proportional to the number of nuclei in a given chemical

environment in a molecule (e.g., if the area under a peak is two times the area under another peak, there are twice as many nuclei responsible for the larger peak than for the smaller one).

- The intensity of an NMR peak gives information about the relative number of a given type of nucleus in a molecule.
- Spin-spin splitting:** In  $^1\text{H}$  NMR, a given hydrogen nucleus interacts with hydrogen nuclei on neighboring carbon atoms such that the peak from that nucleus is split into multiple peaks called a *multiplet*. If a hydrogen nucleus has  $n$  hydrogen nuclei on adjacent atoms, its NMR signal is split into  $(n + 1)$  separate peaks. Relative intensities of the peaks in a multiplet follow *Pascal's triangle*.
    - Spin-spin splitting gives information about the hydrogen atoms neighboring a given hydrogen nucleus.

MULTIPLETS AND PASCAL'S TRIANGLE			
No. of neighboring atoms	Relative intensities of split peaks	Name of multiplet	Splitting pattern
0	1	singlet	
1	1 1	doublet	
2	1 2 1	triplet	
3	1 3 3 1	quartet	
4	1 4 6 4 1	quintet	



## IR SPECTROSCOPY

### A. Theory

- Covalent bonds are similar to springs—bonded atoms vibrate (i.e., stretch and compress) and bend about their bonds. As a consequence of quantum mechanics, these bonded atoms can vibrate and bend only at frequencies that are integral multiples of a fundamental frequency that depends on the type of bond.
- Bonds about which vibration and bending occur can absorb light if the frequency of the light wave is the same as the frequency of the movement about the bond. The frequency of light absorbed by these bonds is generally in the infrared region of the EM spectrum.

3. In IR spectroscopy, a chemical sample is irradiated with infrared light over a wide range of frequencies, and the light absorbed by the sample at each frequency is measured.

4. Bonds about which a molecule is symmetric cannot absorb IR light, and therefore cannot be detected by IR spectroscopy.

### B. Features of an IR spectrum

- IR spectra are displayed as plots of absorption versus wave-number ( $\bar{\nu}$  [ $\text{cm}^{-1}$ ];  $\bar{\nu} = 1/\lambda$ ), which is another measure of the energy of a light wave (similar to frequency). Peaks in an IR spectrum represent wavelengths at which light was absorbed by the molecules in the sample.
- Because each functional group that is IR-active has a characteristic set of frequencies at which it absorbs IR light, IR spectroscopy is useful in detecting the presence of specific functional groups in a molecule.
- Because nearly all organic molecules contain C-C and C-H bonds that absorb IR light in similar ways, IR spectroscopy is most useful in identifying functional groups that contain other bonds besides C-C and C-H bonds.
- Fingerprint region:** Region between  $1200\text{cm}^{-1}$  and  $1700\text{cm}^{-1}$  in an IR spectrum; contains complicated absorption peaks that are characteristic of a specific molecule. An unknown compound can be identified with reasonable certainty if its fingerprint region matches that of a known compound.

## UV/VIS SPECTROSCOPY

### A. Theory

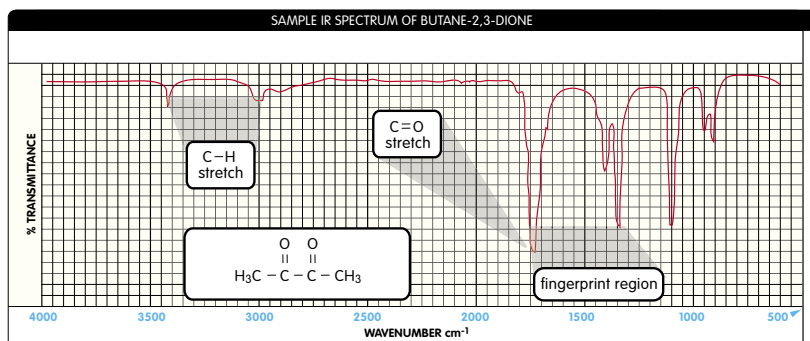
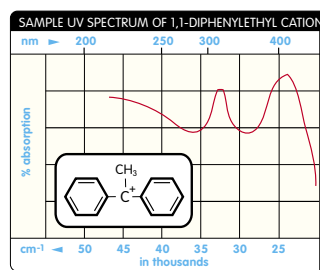
- If a molecule has  $\pi$  electrons, it can absorb UV or visible light to promote one of those electrons into a higher-energy orbital.
- UV/Vis spectroscopy generally involves the promotion of the  $\pi$  electron in the highest-energy occupied orbital to the lowest-energy unoccupied orbital.
- A UV/Vis spectrum is taken by irradiating a sample with UV/Vis light over a range of wavelengths and measuring the amount of light absorbed at each wavelength.

### B. Features of a UV/Vis spectrum

- UV/Vis spectra are displayed as plots of absorption versus wavelength. Peaks represent wavelengths at which light was absorbed by the molecules in the sample.
- The energy of the UV/Vis light absorbed by a  $\pi$  electron system in a molecule depends on the nature of the  $\pi$  system. As a result, the presence of a particular type of  $\pi$  system in a molecule can be identified by UV/Vis spectroscopy.
- The energy gap between the highest-energy occupied orbital and the lowest-energy unoccupied orbital decreases as the size of the  $\pi$  electron system increases. Consequently, the wavelength of UV/Vis light absorbed by a molecule increases as the size of its conjugated  $\pi$  electron system increases (because the energy of a light wave decreases with increasing wavelength).
- UV/Vis spectroscopy is generally used on conjugated hydrocarbon systems, but other molecules containing  $\pi$  electron systems, such as carbonyls, are also weak absorbers of UV/Vis light.

TABLE OF CHEMICAL SHIFTS		
$^{13}\text{C}$ NMR CHEMICAL SHIFTS		
	191-206ppm	50-86ppm
	112-172	40-58
	100-150	28-60
	74-96	22-38
$^1\text{H}$ NMR CHEMICAL SHIFTS		
	10.1-12.8ppm	0.8-5.3ppm
	9.2-9.9	2.5-4.4
	6.8-8.3	2.0-3.0
	5.1-8.3	2.0-3.0
		0.7-2.8
	4.3-7.1	1.0-2.0

INFRARED ABSORBANCES FOR COMMON FUNCTIONAL GROUPS					
Wavenumber	Wavelength	Wavenumber	Wavelength		
C-O-H	3000-3500 $\text{cm}^{-1}$	2.9-3.3 $\mu\text{m}$	-C≡N-	2200-2400 $\text{cm}^{-1}$	4.3-4.5 $\mu\text{m}$
R-N-H	3000-3500	2.9-3.3	-C≡C-	2200-2400	4.3-4.5
	3000-3300	3.0-3.3		1680-1840	5.4-5.9
-C≡C-H	3000-3300	3.0-3.3		1550-1680	5.9-6.5
	2850-3000	3.3-3.5		1550-1680	5.9-6.5
				1080-1210	8.3-9.4



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