

Organic Chemistry II

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Reference Material

This section contains material from organic chemistry I. Any material I had to go back and reference at least once in order to complete a problem will be added, as well as some things I think might be useful.

Common Patterns

► Associated Patterns for Oxygen

- A negative (\ominus) charge corresponds with 1 bond and 3 lone pairs.
- The absence of charge corresponds with 2 bonds and 2 lone pairs.
- A positive (\oplus) charge corresponds with 3 bonds and 1 lone pair.

► Associated Patterns for Nitrogen

- A negative charge corresponds with 2 bonds and 2 lone pairs.
- The absence of charge corresponds with 3 bonds and 1 lone pair.
- A positive charge corresponds with 4 bonds and 0 lone pairs.

Hydrogen Deficiency Index

- **Hydrogen deficiency index (HDI):** the measure of degrees of unsaturation.
 - E.g., two degrees of unsaturation results in a HDI of 2.
 - Degrees of freedom help represent possible structures, indicating possible double bonds, triple bonds, rings, or various combinations of each.
 - Only helpful when molecular formula is known for certainty.
- Formula: $\text{HDI} = \frac{1}{2}(2C + 2 + N - H - X)$
 - X: halogen atoms.

Nomenclature of Alkanes

- **Alkane:** acyclic (linear structure) saturated hydrocarbons (no π bonds).
 - General chemical formula: $\text{C}_n\text{H}_{2n+2}$

Selecting the Parent Chain

- **Parent chain:** the longest carbon chain in an alkane.
- **Substituents:** branches connected to the parent chain, can be a single atom, groups of atoms, that replace one or more hydrogen atoms.
 - If there is competition between chains of equal length, then choose the chain with the greatest number of substituents.

Parent Names for Alkanes		
Number of Carbons	Parent	Name
1	meth	methane
2	eth	ethane
3	pro	propane
4	but	butane
5	pent	pentane
6	hex	hexane
7	hept	heptane
8	oct	octane
9	non	nonane
10	dec	decane
11	undec	undecane
12	dodec	dodecane
13	tridec	tridecane
14	tetradec	tetradecane
15	pentadec	pentadecane
20	eicos	eicosane
30	triacont	triacontane
40	tetracont	tetracontane
50	pentacont	hectane
100	hect	hectane

Naming Substituents

- **Alkyl groups:** Substituents that are named the same as the parents, but with the added letters "yl".
- When a group is connected to the ring, then the ring is generally treated as the parent.
 - If the ring has fewer atoms than the rest of the structure, then it becomes a substituent.


Naming Complex Substituents

- **Complex substituents:** branched alkyl substituents.
- Begin by numbering carbons going **away** from the parent chain, then name it as if it's a parent chain itself.
 - Complex substituent are placed in parentheses, indicating it as a single substituent of the parent chain.


Names of Alkyl Groups	
Substituent Carbons	Terminology
1	methyl
2	ethyl
3	propyl
4	butyl
5	pentyl
6	hexyl
7	heptyl
8	octyl
9	nonyl
10	decyl

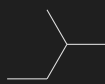
- Some complex substituents have common names that are so well established and allowed by IUPAC.


- An alkyl group bearing **three** carbon atoms; only one way to branch it.

· **Isopropyl group** (1-methylethyl): 

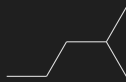
- Alkyl groups bearing **four** carbon atoms, which can be branched three different ways:


· **sec-butyl** (1-methylpropyl): 

· **isobutyl** (2-methylpropyl): 

· **tert-butyl** (1,1-dimethylethyl): 

- Alkyl groups bearing **five** carbons, which can be branched many more ways. Two common ways:

· **isopentyl (isoamyl)** (3-methylbutyl): 

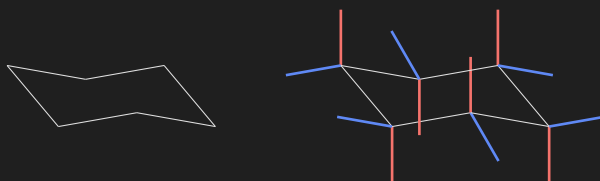
· **neopentyl** (2,2-dimethylpropyl): 

Assembling the Systematic Name

- Locant**: the location of a carbon numbered parent chain.
- Rules for assigning locant:
 - If one substituent is present, then assign the lowest number possible.

- When multiple substituents are present, then the first substituent receives the lowest number.
 - If there is a tie, the second locant should be as low as possible.
 - If tie cannot be broken, then lowest number is assigned alphabetically.
 - Prefixes are used when the same substituent appears more than once.
 - di: 2, tri: 3, tetra: 4, penta: 5, hexa: 6.
 - Hyphens are used to separate numbers from letters, while commas are used to separate numbers from each other.
 - Substituents are alphabeticalized after all locants are correctly assigned.
 - Prefixes are ignored during alphabeticalization.
- Summary of discrete steps:
1. **Identify parent chain.**
 2. **Identify and name substituents.**
 3. **Number the parent chain and assign a locant to each substituent.**
 4. **Arrange the substituents alphabetically.**

Drawing Chair Conformations



- ▷ **Axial position:** parallel to a vertical axis passing through the center of the ring.
 - Axial positions are less stable than equatorial due to steric strain.
- ▷ **Equatorial:** positioned approximately along the equator of the ring.
- ▷ The chair is more stable when the methyl (substituent) group is in the **equatorial** position.
- ▷ The larger the substituent, the more equatorial-substituted conformer is favored.

Overview of Stereoisomerism

- ▷ **Constitutional isomers:** aka structural isomers; same **chemical formula**, but different in the way the **atoms are connected**, i.e., their constitution is different.
- ▷ **Stereoisomers:** isomers that differ in **spatial arrangement** of atoms, rather than connectivity.

- **Geometric isomerism:** aka cis–trans; **locked into spatial positions** due to double bonds or a ring structure.
 - **Cis:** functional groups that are on the **same side** of the carbon chain.
 - **Trans:** functional groups on **opposite sides** of the carbon chain.
 - *Cis-trans* terminology is used to describe disubstituted alkenes (carbon chain with π bond), even when the two substituents are different from each other.
 - Does not apply to disubstituted alkenes in which the substituents are connected in the same position.

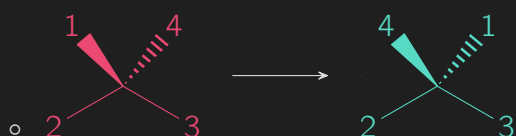
Chirality

- **Superimposable (achiral):** when an object's **mirrored version** is identical to the actual object.
- **Chiral:** objects that are not superimposable.
 - The most common source of molecular chirality is the presence of a carbon bearing **four different groups**.
- **Enantiomer:** the nonsuperimposable mirror image of a chiral compound.
 - Can be used in speech the same way **twin** is used
 - The easiest way to draw enantiomers is to just change wedges and dashes, but there are multiples ways to mirror a molecule, so it can be more complex.
- **Diastereomers:** non-identical stereoisomers (nonsuperimposable) that are **not mirror images** of one another.
 - Enantiomers have the same physical properties, while diastereomers have different physical properties.
 - Differences between enantiomers and diastereomers are especially relevant when comparing compounds with **more than one chiral center**.
 - Maximum number of stereoisomers: 2^n
 - n : number of chiral centers
 - $\frac{2^n}{2}$: pairs of enantiomers.

Cahn-Ingold-Prelog System

- ▷ **Cahn-Ingold-Prelog system:** a system of nomenclature for Identifying each enantiomer individually.
 1. Assign priorities to each of the four groups based on atomic number; the highest atomic number has the highest priority.

2. Rotate the molecule so that the fourth priority group is on a dash (behind)
 3. Determine the configuration, i.e., sequence of 1–2–3 groups.
 - Clockwise (R) or counterclockwise (S).
- ▷ If there is a tie between the atoms connected, then continue outward until a difference is found.
- Do not add the sum all atomic numbers attached to each atom, just the first in which the atoms differ.
 - Any multiple bonded atom, (2 or 3) is treated as if connected to multiple atoms equal to number of bonds.
- ▷ Switching any two groups on a chiral center will invert the configuration, e.g.,



- Can be done twice without changing configuration, e.g.,



Configuration in IUPAC nomenclature

- The configuration of the chiral center is indicated at the beginning of the name, italicized, and surrounded by parentheses.
- When multiple centers are present, then each must be preceded by a locant.

Optical Activity

- ▷ Enantiomers exhibit identical physical properties, but different behavior to plane-polarized light.
- **Polarization:** the orientation of electric field of the electromagnetic wave.
 - **Plane-polarized light:** a filter that only allows light of a particular polarization through.
- ▷ **Optically active:** property of compounds that rotate the plane-polarized light.
- Can be measured using a polarimeter.
 - Chiral compounds are optically active, while achiral compounds are not optically active.
- ▷ **Observed rotation:** (α); the rotation of light due to chiral compounds, which depends on the number of molecules light encounters.

- Doubling the concentration or pathlength both double the observed rotation.
- ▷ **Specific rotation:** $[\alpha]$; a standard concentration (1 g/mL) and a standard pathlength (1 dm) that allows for meaningful comparison between compounds.
 - $[\alpha] = \frac{\alpha}{cl}$
 - c: concentration, l: pathlength.
 - Temperature (T) and wavelength (λ) both have a nonlinear relationship, so it is often noted as: $[\alpha]_{\lambda}^T$
- ▷ Specific rotation for enantiomers are equal in magnitude but opposite in direction.
 - **Dextrorotatory:** a compound exhibiting positive rotation.
 - **Levorotatory:** a compound exhibiting negative rotation.
 - No direct relationship between R/S system of nomenclature, as that is independent of conditions, but dependent on observation angle.
 - The direction of polarized light, however, is dependent on conditions, and can change based on temperature or wavelength even with the same given configuration.

Enantiomeric Excess

- **Optically (enantiomerically) pure:** a solution containing a single enantiomer.
- **Racemic mixture:** a solution containing equal amounts of both enantiomers, resulting in an optically inactive appearance.
- **Enantiomeric excess (ee):** when a solution containing both enantiomers in unequal amounts, appearing optically active.

$$\bullet \% ee = \frac{|\text{observed } (\alpha)|}{|\text{specific } [\alpha]|} \times 100\%$$

Symmetry and Chirality

- ▷ Any compound with a single chiral center must be chiral, however, the same is not always true for two or more.
- ▷ **Reflectional symmetry:** when an object has a plane of symmetry that can be reflected across and still generate the same image.
 - Any compound that possesses a plane of symmetry in any conformation will be achiral.
- ▷ **Rotational symmetry:** when an object has an axis of symmetry, i.e., it can be rotated around a single point and appear 2 or more times.
 - Order: how many times the object appears.

- Chirality is **not dependent** on rotational symmetry.
- ▷ **Point symmetry (inversion)**: when every part of an object has a matching part, i.e., **equal distance** from the **central point**, but in **opposite direction**.
 - Absence of a plane of symmetry does not mean it is chiral.
 - If a compound exhibits **inversion**, then it is **achiral**.
- ▷ Summary of relationship between symmetry and chirality:
 - The presence of absence of rotational symmetry is irrelevant to chirality.
 - A compound that has a plane of symmetry will be achiral.
 - A compound that lacks a plane of symmetry will most likely be chiral, with some exceptions.
- ▷ **Meso compounds**: achiral compounds (posses plane of symmetry or can be inverted) that have multiple chiral centers.
 - A family of stereoisomers containing a meso compound will have less than 2^n stereoisomers.

Fischer Projections

- **Fischer projections**: two-dimensional representations of organic molecules by projection.
 - Limited to carbohydrates/sugars with multiple chiral centers.
- **Horizontal** lines are considered to be coming **out** of the page.
- **Vertical** lines are considered to be going **behind** the page.
- Helpful for quickly comparing relationship between stereoisomers with multiple chiral centers;
 - Enantiomers will have opposite configurations, while diastereomers will not.
 - Assuming the north is priority 2, and the south is priority 3:
 - If the atom with priority 1 is on the **right**, then it will have an **R** configuration.
 - If the atom with priority 1 is on the **left**, then it will have an **S** configuration.