

- I. FUNCTIONAL GROUPS:** Functional groups with similar structure/reactivity may be "grouped" together.
- A. Functional Groups With Carbon-Carbon Multiple Bonds
 - 1. Alkenes
 - 2. Alkynes
 - 3. Arenes (Aromatic Compounds)
 - B. Functional Group With Carbon Singly Bonded To An Electronegative Element
 - 1. Alkyl Halides
 - 2. Alcohols
 - 3. Ethers
 - 4. Amines
 - 5. Thiols
 - 6. Sulfides
 - C. Functional Groups With A Carbon-Oxygen Double Bond
 - 1. Aldehydes
 - 2. Ketones
 - 3. Carboxylic Acids
 - 4. Esters
 - 5. Amides
 - 6. Acid Chlorides
 - 7. Anhydrides

II. ALKANES (also called aliphatic, saturated hydrocarbons, paraffins) (**Section 2.1-2.3**)

Alkanes are organic compounds that contain only sp^3 carbon atoms and hydrogen atoms. Alkanes can be classified into three groups.

- A. STRAIGHT CHAIN OR NORMAL ALKANES
 - 1. The general molecular formula for a straight chain alkane is: C_nH_{2n+2} .
 - 2. The lower case letter "n" is written before the molecular formula in a straight chain alkane.
- B. BRANCHED CHAIN ALKANES: Branched chain alkanes are isomers of straight chain alkanes, i.e., same molecular formula but different chemical structure.
- C. CYCLOALKANES: Cycloalkanes (alicyclic) alkanes form ring-like structures.

III. NOMENCLATURE OF ALKANES (**Section 2.2-2.3**)

- A. GENERAL NOMENCLATURE: Organic compounds are named according to IUPAC rules
 - 1. PREFIX: Specifies the functional group or substituent position on the parent carbon chain.
 - 2. PARENT: Indicates how many carbon atoms are in the "main" chain of the compound. The main chain is defined as the longest continuous carbon chain.
 - 3. SUFFIX: Identifies the functional group(s) represented in the molecule.
- B. IUPAC RULES FOR NAMING ALKANES
 - 1. Find the parent hydrocarbon, i.e., the longest continuous carbon chain. Parent name is based on the number of carbon atoms in the chain; use Greek name.
 - 2. Number the carbon atoms in the main chain so that substituents on the main chain have the lowest possible numbers.
 - 3. Identify and number the substituents.
 - 4. Substituents are placed in alphabetical order.
 - 5. The suffix used for alkanes is "ane"
 - 6. Write out the name as a single word with numbered substituents first, using commas to separate numbers and hyphens to separate different prefixes.
- C. NAMING ALKYL GROUPS (i.e., Alkanes as substituents)
 - 1. A generic name for an alkane that is a substituent on a longer parent chain is called an "alkyl group". Alkyl groups are represented as "R"
 - 2. Alkyl groups are named by replacing the "ane" of the corresponding alkane with a "yl" suffix.
 - 3. There are some common names for alkyl substituents.
- D. NAMING CYCLOALKANES
 - 1. The prefix "cyclo" is added the parent portion of the alkane name.

2. The stereochemistry of a substituted cycloalkane is indicated by including the prefix "cis" or "trans" at the beginning of the cycloalkane name.
- E. DEGREE OF ALKYL SUBSTITUTION: The degree of alkyl substitution refers to how many other carbon atoms a particular carbon atom is bonded to. Carbon atoms can be classified into four groups according to their degree of alkyl substitution.
1. PRIMARY CARBON (1°): Bonded to one other *carbon*.
 2. SECONDARY CARBON (2°): Bonded to two other *carbons*
 3. TERTIARY CARBON (3°): Bonded to three other *carbons*
 4. QUARTERNARY CARBON (4°): Bonded to four other *carbons*

II. NOMENCLATURE OF ALKYL HALIDES, ETHERS, ALCOHOLS & AMINES (Section 2.4-2.7)

A. ALKYL HALIDES

1. Alkyl halides contain a halogen bonded to an sp^3 hybridized carbon atom.
2. Alkyl halides can be classified as primary, secondary or tertiary depending on the substitution of the carbon atom that bears the halogen.
3. Alkyl halides are named using IUPAC rules where the halogen is treated as a substituent on the parent chain, i.e., iodomethane.
4. Alkyl halides are named using a "common" system where the alkyl portion of the molecule is treated as the substituent and the halogen as the parent, i.e., methyl iodide.

B. ETHERS

1. An ether is an organic compound that has an oxygen atom bonded to two carbon atoms (alkyl, aryl, vinyl). The oxygen and carbon atoms of ethers are sp^3 hybridized.
2. Ethers may have symmetrical or unsymmetrical structures.
3. Ethers can be named in two ways.
 - a. Combine the two carbon atom substituents and add the word "ether" to the end.
 - b. Ethers can be named as an alkoxy substituent on a parent compound.
4. A cyclic ether has the ether oxygen atom as part of a ring.
 - a. A 3-membered ring ether is called an epoxide or oxirane.
 - b. A 4-membered ring ether is called an oxetane
 - c. A 5-membered ring ether is called a furan or oxolane.
 - d. A 6-membered ring ether is called a pyran or oxane.
5. Cyclic ethers are named with the above parent names and are numbered starting at the oxygen atom, i.e., oxygen is number 1.
 - a. The parent name of five and six-membered ring ethers are for the unsaturated systems. The corresponding saturated systems are ...
 - i. Furan: 2 double bonds; Dihydrofuran: 1 double bond; Tetrahydrofuran: 0 double bonds.
 - b. Epoxides are the most reactive of all cyclic ethers.

C. ALCOHOLS

1. Alcohols are compounds with a hydroxy group bonded to an sp^3 hybridized carbon atom.
2. Alcohols are classified as primary, secondary or tertiary based on the C bonded to the OH
3. The parent of an alcohol is the longest continuous carbon chain which contains the carbon atom bonded to the -OH group
4. Alcohols are named by using an "-ol" suffix with a hydrocarbon parent
5. The parent chain is numbered so as to give the carbon atom bonded to the -OH group the lowest possible number. A number corresponding to the position of the OH group on the parent chain is included in the name as a prefix.
6. There are a number of alcohols with common names.

D. AMINES

1. Amines are organic functional groups that contain an sp^3 N bonded to C or H that are not bonded to any other heteroatoms.

2. Amines are classified as primary, secondary or tertiary based on the # carbon atoms bonded to the N
3. The parent of an amine is the longest continuous carbon chain which contains the N atom
4. The parent chain is numbered so as to give the carbon atom bonded to the N atom the lowest possible number. A number corresponding to the position of the N on the parent chain is included in the name as a prefix.
5. The suffix "amine" is used.
6. Primary amines may also be named as amino substituted alkanes. The -NH_2 group is referred to as an amino substituent.
7. For secondary and tertiary amines, the prefix "N-" is used to indicate the alkyl substituents on the amine parent.

III. PROPERTIES OF ALKANES, ALKYL HALIDES, ETHERS, ALCOHOLS & AMINES (Section 2.9)

A. ALKANES

1. Alkanes are generally chemically inert and non-polar.
2. The boiling point and melting point of an alkane increases with increasing molecular weight.
3. The boiling point of a branched chain alkane is generally lower than its straight chain isomer.

B. ALKYL HALIDES

1. Alkyl halides contain a polar covalent bond.
2. Alkyl halides are more polar than alkanes.

C. ETHERS

1. Ethers have two polar covalent bonds. Most ethers are polar molecules.
2. Ethers can be involved in hydrogen bonding & dipole-dipole interactions.

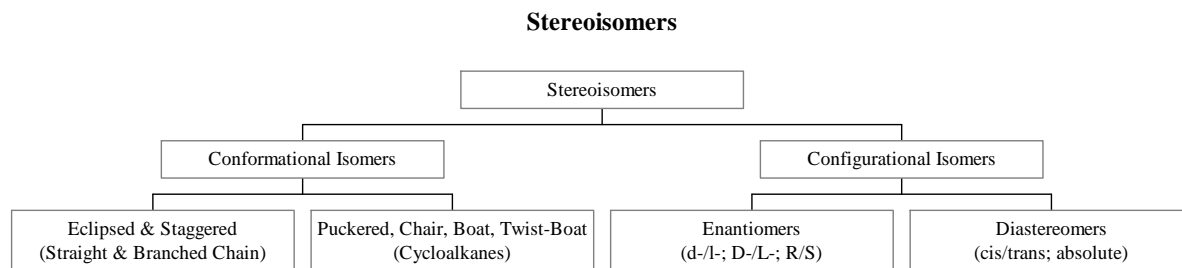
D. ALCOHOLS

1. Alcohols can participate in H-bonding between the "positive" H end of the -OH bond and the "negative" O end of the -OH bond of different alcohol molecules.
2. Alcohols are amphoteric
 - i. Alcohols are acidic compounds because they can donate a proton to a base. When an alcohol becomes deprotonated the resulting species is called an alkoxide.
 - ii. Alcohols can also behave as bases and accept a proton to form an oxonium ion.

E. AMINES

1. Amines are basic functional groups
 - a. The pK_a of an amine refers to its conjugate acid
 - b. pK_a values for alkyl amines range from 7-11 and for aromatic amines from 1-5 (due to resonance)
2. Amines are nucleophilic
3. Amines can undergo H-bonding

IV. STEREOCHEMISTRY



V. CONFORMERS OF ALKANES (Section 2.10)

Conformers are isomers which arise due to rotation about a carbon-carbon single bond.

- A. Conformers of alkanes can be represented in two ways.
 1. SAWHORSE REPRESENTATION
 2. NEWMAN PROJECTION

- B. Newman projections help to predict the energy required to rotate about a C-C single
 - 1. Conformers of ethane
 - a. Eclipsed conformation (Torsional strain)
 - b. Staggered conformation
 - 2. Conformers of propane
 - a. Eclipsed conformation (Torsional strain)
 - b. Staggered conformation
 - 3. Conformers of butane
 - a. Eclipsed conformation (2 forms, Torsional strain)
 - b. Anti conformation
 - c. Gauche conformation (Steric strain)

VI. CONFORMERS OF CYCLOALKANES (Section 2.11)

180° Rotation about the C-C bonds in cycloalkanes DOES NOT OCCUR due to the constraints of the ring. Some (i.e., < 180°) rotation can occur however which can lead to conformational isomers of cycloalkanes.

- A. Three types of strain energies are associated with cycloalkane conformers.
 - 1. TORSIONAL STRAIN (Eclipsing Interactions)
 - 2. STERIC STRAIN (Gauche Interactions)
 - 3. ANGLE STRAIN (Bond angle distortion)
- B. The degree of strain encountered by a cycloalkane is dependent on the size of the ring.
 - 1. CYCLOPROPANE
 - 2. CYCLOBUTANE
 - 3. CYCLOPENTANE
 - 4. CYCLOHEXANE
- C. Disubstituted cycloalkanes give rise to cis/trans stereoisomers.

VII. CONFORMERS OF CYCLOHEXANE: There are 3 conformations of cyclohexane. (Section 2.12-2.14)

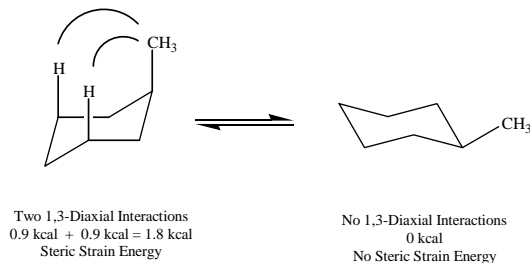
- A. CHAIR CONFORMATION
 - 1. The chair conformation of cyclohexane is strain-free.
 - 2. There are two chair forms of cyclohexane which can be interconverted via a "ring flip".
 - 3. There are two types of substituents on a chair conformation relative to the ring.
 - a. AXIAL SUBSTITUENTS: "Perpendicular" to the ring
 - b. EQUATORIAL SUBSTITUENT: "Parallel" to the ring
 - 4. For substituted cyclohexanes, interactions between substituents on the ring cause steric strain.
 - i. 1,3-DIAXIAL SUBSTITUENTS
 - ii. 1,2-EQUATORIAL SUBSTITUENTS
- 2. BOAT CONFORMATION
 - a. There is no angle strain associated with the boat conformation of cyclohexane.
 - b. There is steric strain between carbons 1 and 4.
 - c. There is torsional strain between eclipsing hydrogens on carbons 2,3,5,6.
- 3. TWIST BOAT CONFORMATION

1,3-Diaxial Interactions	Energy (kcal/mol)
H- and -CH ₃	0.9 kcal
H- and CH ₃ CH ₂ -	1.0 kcal
H- and isopropyl	1.1 kcal
H- and phenyl	1.5 kcal
H- and t-butyl	2.7kcal
-CH ₃ and -CH ₃	4.5 kcal

VIII. CONFORMATIONAL ANALYSIS OF CYCLOHEXANES

A. MONOSUBSTITUTED CYCLOHEXANES

1. Axial and equatorial conformers



2. Equilibrium between axial and equatorial conformers.

- Equatorial conformers are more stable than axial conformers.
- Keq can be determined using Free energy equation and steric strain energies for each conformer
- The percent of each chair conformation at a given temperature at equilibrium can also be calculated

$$\begin{aligned}\Delta G^\circ &= E_P - E_R \\ &= 0 - 1.8 \\ &= -1.8 \text{ kcal}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= -RT \ln Keq \\ -1.8 \text{ kcal} &= \frac{(1.98 \text{ kcal/K} \cdot \text{mol})(298)}{\ln Keq}\end{aligned}$$

$$\begin{aligned}R &= 1.98 \text{ cal/K} \cdot \text{mol} \\ T \text{ (in Kelvin)} &= 25^\circ\text{C} + 273 = 298\end{aligned}$$

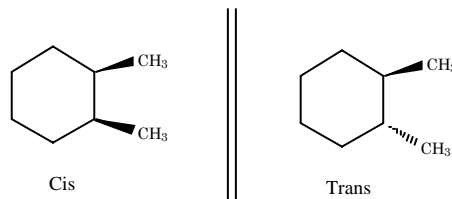
$$\begin{aligned}1000 \\ -1.8 \text{ kcal} &= -0.59 \ln Keq \\ 1.8 \text{ kcal} &= 0.59 \ln Keq \\ 1.21 &= \ln Keq \\ Keq &= 3.32\end{aligned}$$

$$\begin{aligned}Keq &= P/R & 100\% &= P + R \\ 3.32 &= P/R & 100\% &= 3.32R + R \\ 3.32R &= P & 100\% &= 4.32R \\ & & 100/4.32 &= R \\ & & 23\% &= R\end{aligned}$$

$$\begin{aligned}100 - R &= P \\ 100 - 23 &= P \\ 77\% &= P\end{aligned}$$

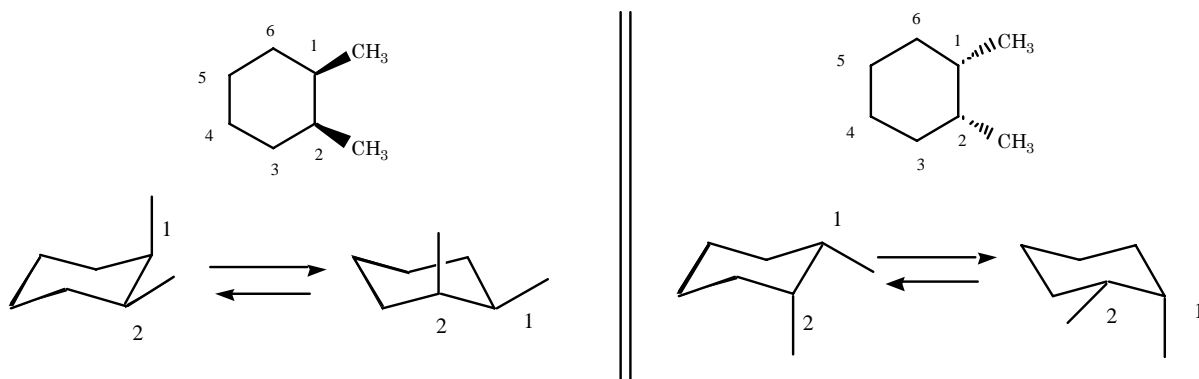
B. DISUBSTITUTED CYCLOHEXANES

1. Disubstituted cyclohexanes can have cis or trans stereochemistry.



2. There are two chair conformations of cis and two chair conformations of trans cyclohexanes

Cis



Trans

