

Chapter 4

Alkanes: Nomenclature, Conformational Analysis, and an Introduction to Synthesis

Alkanes = saturated hydrocarbons

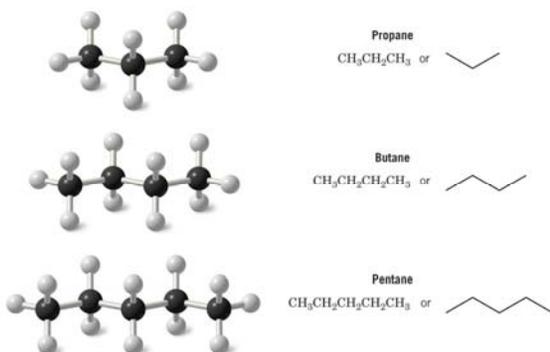
Simplest alkane = methane CH_4

We can build additional alkanes by adding $-\text{CH}_2-$ units

$\text{C}_n\text{H}_{2n+2}$ = saturated = no double bonds, no rings

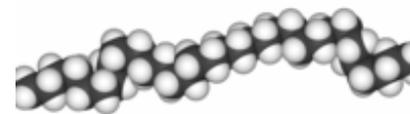
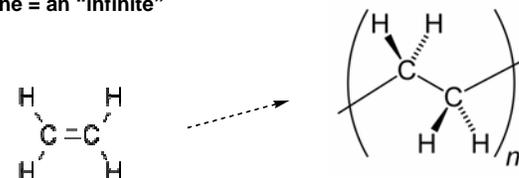
Shapes of Alkanes

“Straight-chain” alkanes have a zig-zag orientation when they are in their most straight orientation



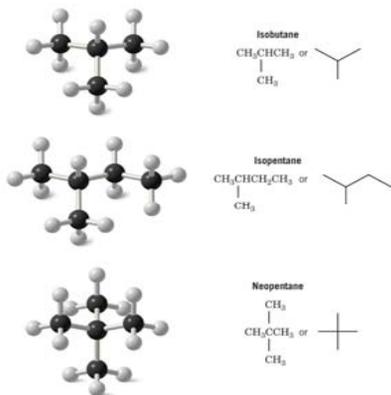
There is no limit on length of chain

Polyethylene = an “infinite”
alkane



Branched alkanes

At least one carbon attached to more than two others



Many constitutional isomers are possible

Same molecular formula but different connectivity of atoms
 Constitutional isomers have different physical properties
 (melting point, boiling point, densities etc.)

5
 "hexanes"
 C_6H_{14}

Structural Formula	mp (°C)	bp (°C) ^a (1 atm)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-95	68.7
$\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3$ CH_3	-153.7	60.3
$\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3$ CH_3	-118	63.3
$\text{CH}_3\text{CH}-\text{CHCH}_3$ CH_3 CH_3	-128.8	58
$\text{CH}_3-\text{C}-\text{CH}_2\text{CH}_3$ CH_3	-98	49.7

The number of constitutional isomers possible for a given molecular formula rise rapidly with the number of carbons

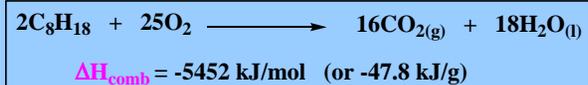
Molecular Formula	Possible Number of Constitutional Isomers
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$\text{C}_{10}\text{H}_{22}$	75
$\text{C}_{15}\text{H}_{32}$	4,347
$\text{C}_{20}\text{H}_{42}$	366,319
$\text{C}_{30}\text{H}_{62}$	4,111,846,763
$\text{C}_{40}\text{H}_{82}$	62,481,801,147,341

A reaction of alkanes - Combustion

All hydrocarbons are combustible

Combine with oxygen and release energy

Heat of combustion is very high



IUPAC Nomenclature

- Early chemicals were given “common” or “trivial” names based on the source of the compound or a physical property
- The **International Union of Pure and Applied Chemistry (IUPAC)** started devising a systematic approach to nomenclature in 1892
- The fundamental principle in devising the system was that each different compound should have a **unique, unambiguous name**
- The basis for all IUPAC nomenclature is the set of rules used for naming alkanes

● Nomenclature of Unbranched Alkanes **Learn the first ten!**

Name	Number of Carbon Atoms	Structure
Methane	1	CH ₄
Ethane	2	CH ₃ CH ₃
Propane	3	CH ₃ CH ₂ CH ₃
Butane	4	CH ₃ (CH ₂) ₂ CH ₃
Pentane	5	CH ₃ (CH ₂) ₃ CH ₃
Hexane	6	CH ₃ (CH ₂) ₄ CH ₃
Heptane	7	CH ₃ (CH ₂) ₅ CH ₃
Octane	8	CH ₃ (CH ₂) ₆ CH ₃
Nonane	9	CH ₃ (CH ₂) ₇ CH ₃
Decane	10	CH ₃ (CH ₂) ₈ CH ₃
Undecane	11	CH ₃ (CH ₂) ₉ CH ₃
Dodecane	12	CH ₃ (CH ₂) ₁₀ CH ₃
Tridecane	13	CH ₃ (CH ₂) ₁₁ CH ₃
Tetradecane	14	CH ₃ (CH ₂) ₁₂ CH ₃
Pentadecane	15	CH ₃ (CH ₂) ₁₃ CH ₃
Hexadecane	16	CH ₃ (CH ₂) ₁₄ CH ₃

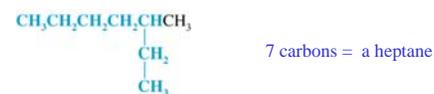
Nomenclature of Unbranched Alkyl groups

The unbranched alkyl groups are obtained by removing one hydrogen from the alkane and named by replacing the -ane of the corresponding alkane with -yl

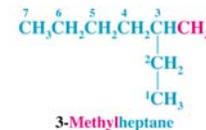
ALKANE		ALKYL GROUP	ABBREVIATION
CH ₃ —H Methane	becomes	CH ₃ — Methyl	Me—
CH ₃ CH ₂ —H Ethane	becomes	CH ₃ CH ₂ — Ethyl	Et—
CH ₃ CH ₂ CH ₂ —H Propane	becomes	CH ₃ CH ₂ CH ₂ — Propyl	Pr—
CH ₃ CH ₂ CH ₂ CH ₂ —H Butane	becomes	CH ₃ CH ₂ CH ₂ CH ₂ — Butyl	Bu—

Nomenclature of Branched-Chain Alkanes (IUPAC)

- Locate the longest continuous chain of carbons; this is the parent chain and determines the parent name.

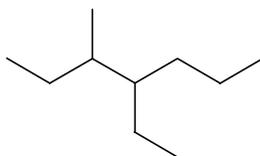


- Number the longest chain beginning with the end of the chain nearer the substituent.
- Designate the location of the substituent.



Nomenclature of Branched-Chain Alkanes (IUPAC) – cont.

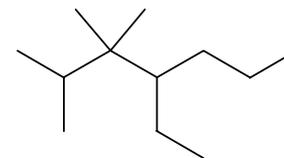
4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain
Substituents are listed alphabetically



4-ethyl-3-methylheptane

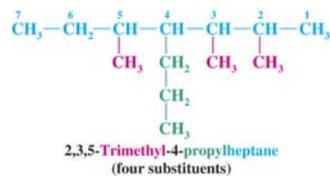
Nomenclature of Branched-Chain Alkanes (IUPAC) – cont.

5. When two or more substituents are identical, use the prefixes *di-*, *tri-*, *tetra-* etc.
a) Commas are used to separate numbers from each other
b) Repeat the number if two substituents on same carbon
c) The prefixes are NOT used in alphabetical prioritization

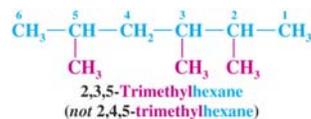


4-ethyl-2,3,3-trimethylheptane

6. When two chains of equal length compete to be parent, choose the chain with the greatest number of substituents.

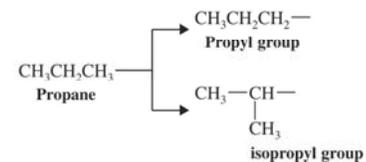


7. When branching first occurs at an equal distance from either end of the parent chain, choose the name that gives the lower number at the first point of difference.

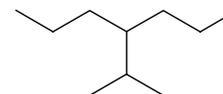


Nomenclature of Branched Alkyl Chains

Two alkyl groups can be derived from propane



Example:



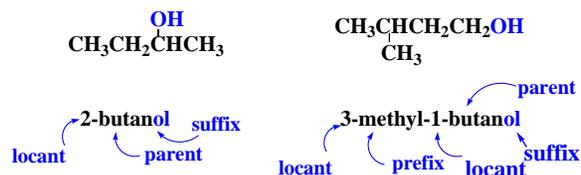
4-isopropylheptane

Nomenclature of Alcohols

In the IUPAC naming system, there may be as many as **four components** to the name:

Parent is the parent alkane.
Prefix names the substituent group
Locant indicates the position of a substituent
Suffix names a key function

Examples



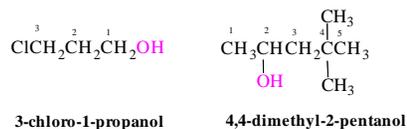
IUPAC Nomenclature of Alcohols

1. Select the longest chain containing the hydroxyl and change the suffix ending of the parent alkane from **-e to -ol**
2. Number the parent to give the hydroxyl the lowest possible number
3. The other substituents take their locations accordingly

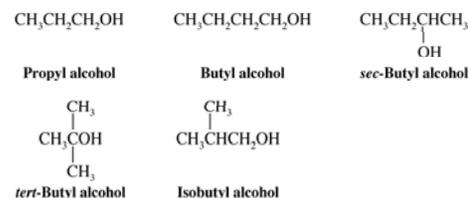


4-methyl-1-hexanol

• Examples



• Common Names of simple alcohols are still often used and are approved by IUPAC



Nomenclature of cycloalkanes

- ◆ Ring compounds are very common
- ◆ Named as cyclo + parent name for number of C's in the ring



cyclobutane



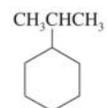
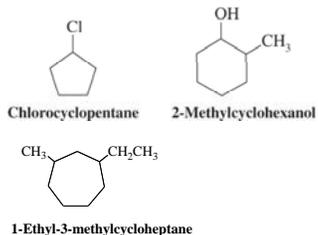
cyclopentane



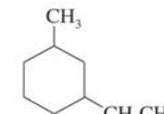
cyclooctane

Nomenclature of Substituted Cycloalkanes

- ◆ If only one substituent is present, it is assumed to be at position one and is not numbered
- ◆ When two or more alkyl substituents are present, the one with alphabetical priority is given position 1
 - Numbering continues - either clockwise or counterclockwise, to give the other substituents the lowest numbers
 - If one of the substituents is a functional group (e.g., hydroxyl) it is given position #1.

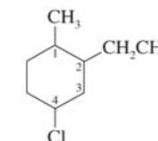


Isopropylcyclohexane



1-Ethyl-3-methylcyclohexane
(not 1-ethyl-5-methylcyclohexane)

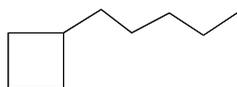
BUT, keep numbers as low as possible!



4-Chloro-2-ethyl-1-methylcyclohexane
(not 1-chloro-3-ethyl-4-methylcyclohexane)

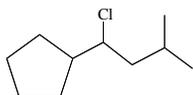
Cycloalkyl group

- ◆ If other parts of the molecule are dominant or if a long chain is attached to a ring with fewer carbons, the cycloalkane is considered the substituent

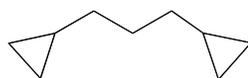


1-cyclobutylpentane

(chain has more carbons than ring)



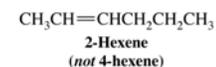
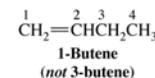
1-chloro-1-cyclopentyl-3-methylbutane



1,3-dicyclopropylpropane

Nomenclature of Alkenes and Cycloalkenes

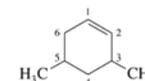
- ◆ Alkenes are named by finding the longest chain containing the double bond and changing the name of the parent alkane from **-ane to -ene**
- ◆ The compound is numbered to give the first alkene carbon the lowest number



- ◆ The double bond of a cycloalkene must be in positions 1 and 2



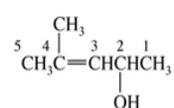
1-Methylcyclopentene
(not 2-methylcyclopentene)



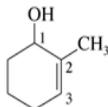
3,5-Dimethylcyclohexene
(not 4,6-dimethylcyclohexene)

Double bonds plus alcohol hydroxyl groups = alkenols

The hydroxyl is the group with higher priority and must be given the lowest possible number



4-Methyl-3-penten-2-ol
or 4-methylpent-3-en-2-ol

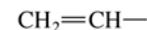


2-Methyl-2-cyclohexen-1-ol
or 2-methylcyclohex-2-en-1-ol

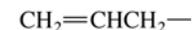
Note that positions of both the C=C and the OH must be indicated

Vinyl and allyl groups

The vinyl and allyl groups are common names that need to be readily recognized:



The vinyl group



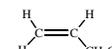
The allyl group



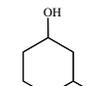
bromoethene
or
vinyl bromide



vinylcyclopropane



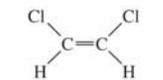
3-chloropropene
or
allyl chloride



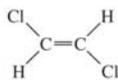
3-allylcyclohexanol

Alkene nomenclature – *cis* and *trans*

- If two groups occur on the **same side** of the double bond the compound is ***cis***
- If they are on **opposite sides** the compound is ***trans***

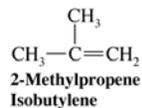
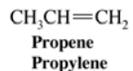
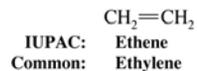


cis-1,2-Dichloroethene



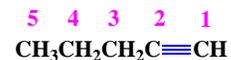
trans-1,2-Dichloroethene

- Several alkenes have common names which are recognized by IUPAC



Alkynes = named similarly to alkenes

- (1) Choose the longest continuous chain of carbons **containing the triple bond**.
- (2) The name of the parent alkane is modified by dropping "ane" and adding "**yne**."
- (3) Number the parent chain from the end **closest to the triple bond**.



1-pentyne

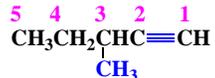


2-butyne

(4) Positions of substituents are determined by the usual rules.



1-chloro-2-butyne



3-methyl-1-pentyne

(5) In an **alkynol**, the alcohol has priority in numbering.



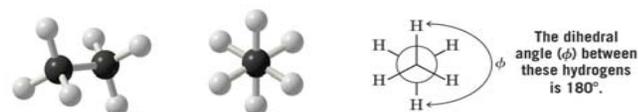
3-butyne-1-ol

1-alkynes are also called terminal alkynes

Terminal alkynes have an acidic H $\text{R}-\text{C}\equiv\text{CH}$ $pK_a = 25$

Sigma Bonds and Bond Rotation

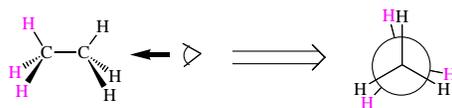
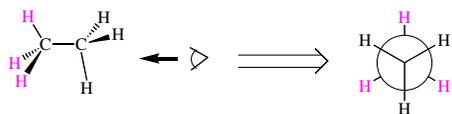
- Ethane has relatively free rotation around the carbon-carbon bond
- The **staggered** conformation has C-H bonds on adjacent carbons as far apart from each other as possible
 - The drawing to the right is called a Newman projection



- The **eclipsed** conformation has all C-H bonds on adjacent carbons directly on top of each other



How to draw a Newman projection



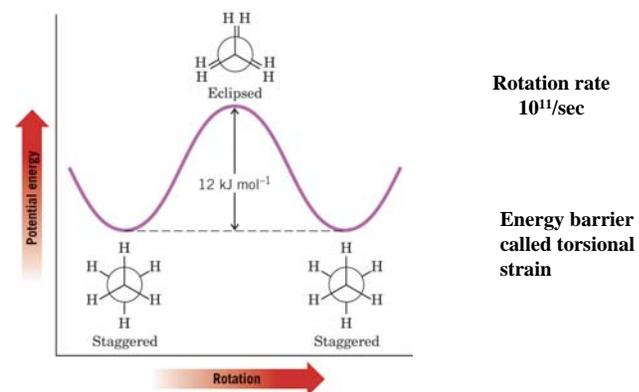
Sight down the C-C bond (sigma bond is symmetric)

Groups on front carbon intersect in center

Groups on back carbon end at circle

The potential energy diagram of the conformations of ethane

The staggered conformation is more stable than eclipsed by 12 kJ mol^{-1}

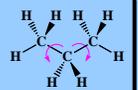


Bond Rotations in Propane

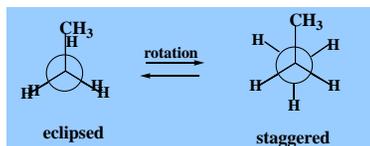
There are 2 equivalent C-C bonds

One can only show one C-C bond at a time.

The conformational features are the same for the two C-C bonds.



Consider as ethane with 1 H replaced by a CH₃

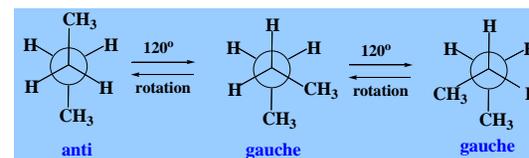
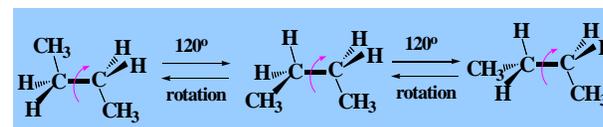


Barrier = 14 kJ/mol

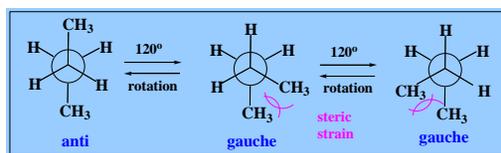
Conformational Analysis of Butane

Rotation around C₂-C₃ of butane gives three energy minima

The two **gauche** conformations are less stable than the **anti** conformation by 3.8 kJ mol⁻¹ because of repulsive Van der Waals forces between the two methyl groups.



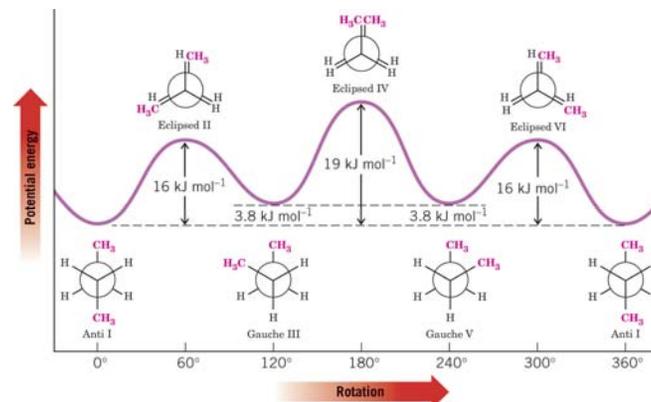
The Staggered Conformations of Butane (cont'd)



The staggered **anti** is more stable than the two equivalent staggered **gauche** conformations. In the anti conformation, the two CH₃ groups are on opposite sides of the structure. In the gauche conformations, the two groups are within van der Waals repulsive interaction distance, and 3.8 kJ/mol of steric strain energy is introduced.

Conformational Analysis of Butane

3 minima and energy barriers between each (3 maxima)



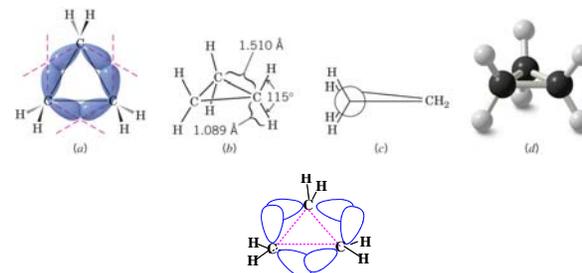
Relative Stabilities of Cycloalkanes: Ring Strain

- Heats of combustion per CH₂ unit reveal cyclohexane has no ring strain and other cycloalkanes have some ring strain

Cycloalkane (CH ₂) _n	n	Heat of Combustion (kJ mol ⁻¹)	Heat of Combustion per CH ₂ Group (kJ mol ⁻¹)	Ring Strain (kJ mol ⁻¹)
Cyclopropane	3	2091	697.0	115
Cyclobutane	4	2744	686.0	109
Cyclopentane	5	3320	664.0	27
Cyclohexane	6	3952	658.7	0
Cycloheptane	7	4637	662.4	27
Cyclooctane	8	5310	663.8	42
Cyclononane	9	5981	664.6	54
Cyclodecane	10	6636	663.6	50
Cyclopentadecane	15	9885	659.0	6
Unbranched alkane	—	—	658.6	—

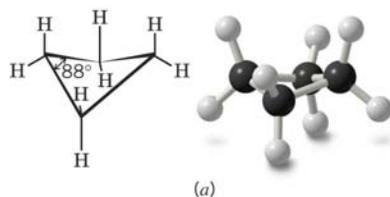
The Origin of Ring Strain in Cyclopropane : Angle Strain and Torsional Strain

- Angle strain** is caused by bond angles different from 109.5°
 - C-C angle of 60 means orbital overlap is reduced
- Torsional strain** is caused by eclipsing C-H bonds on adjacent C's
 - Cyclopropane has both high angle and torsional strain



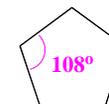
Cyclobutane: Angle Strain and Torsional Strain

- Cyclobutane has considerable angle strain (but not as much as in cyclopropane).
- Cyclobutane bends to relieve some torsional strain, even though bending increases angle strain (90° becomes 88°)



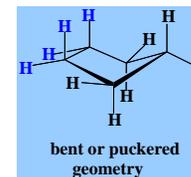
Cyclopentane

The internal angles of a regular pentagon are 108°, close to the idealized tetrahedral bond angles. Thus, a **planar cyclopentane** would have very little angle strain.



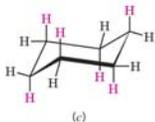
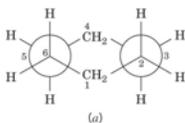
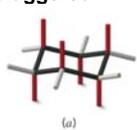
But a planar geometry would have **very severe torsional strain** (10 eclipsed H). Consequently, the geometry of cyclopentane is bent.

The torsional strain is reduced in the bent structure. **Four H** are still eclipsed, but 6 are staggered.



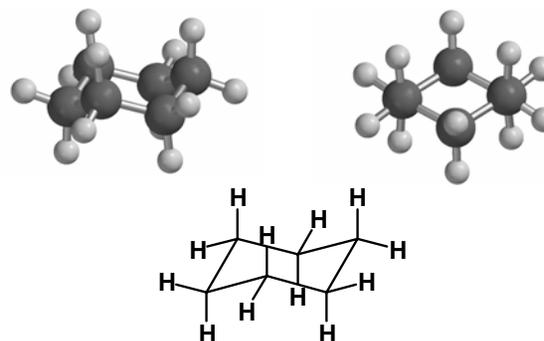
Cyclohexane: the perfect ring

- ◆ Cyclohexane is not planar, since the angle of a simple hexagon is 120° .
- ◆ Cyclohexane adopts a **CHAIR CONFORMATION** that has **no ring strain** and **no angle strain**!
- ◆ All bond angles are 109.5° and all C-H bonds are perfectly staggered



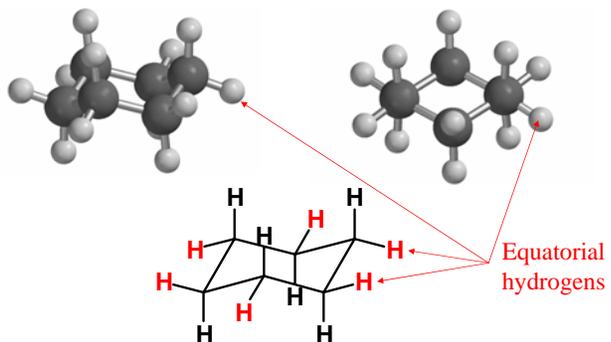
Conformations of Cyclohexane

“Chair” conformation



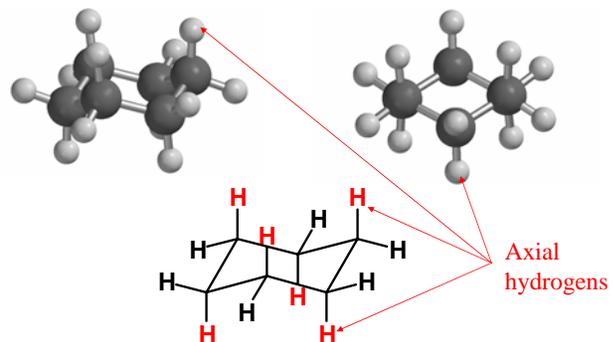
Conformations of Cyclohexane

“Chair” conformation



Conformations of Cyclohexane

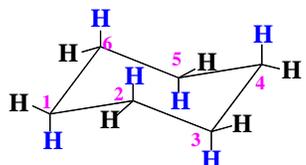
“Chair” conformation



Two types of H in chair cyclohexane

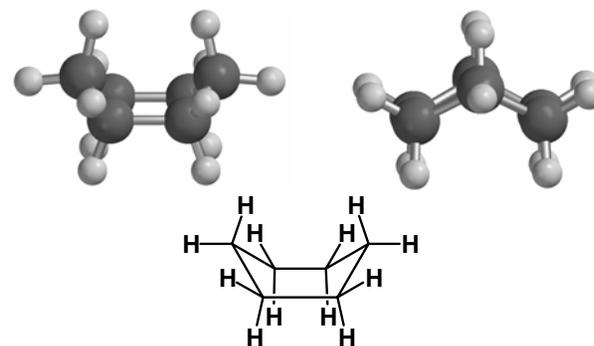
6 H are **axial**
(up and down)

6 H are **equatorial**
(close to plane of ring)



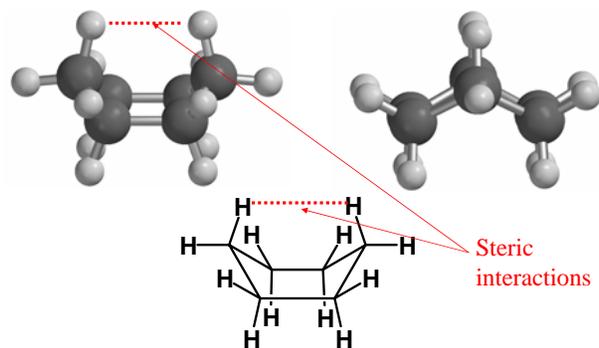
Conformations of Cyclohexane

“Boat” conformation



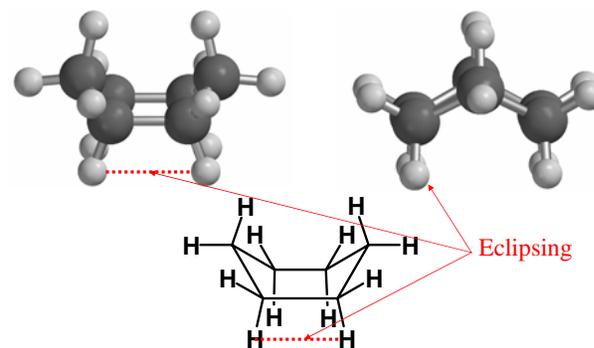
Conformations of Cyclohexane

“Boat” conformation



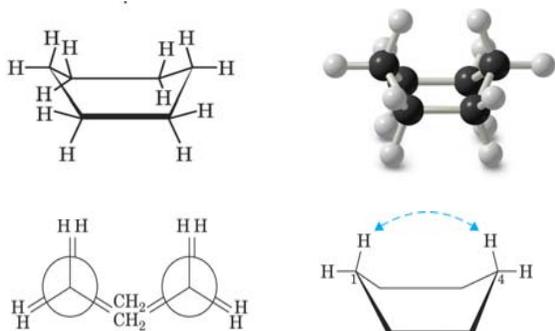
Conformations of Cyclohexane

“Boat” conformation



Rotation about single bonds flips the ring to a boat form

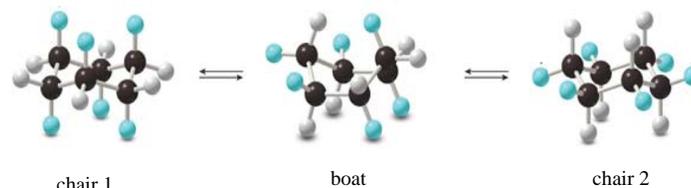
- The boat conformation is less stable because of flagpole interactions and torsional strain along the bottom of the boat



Ring flipping leads to a second chair

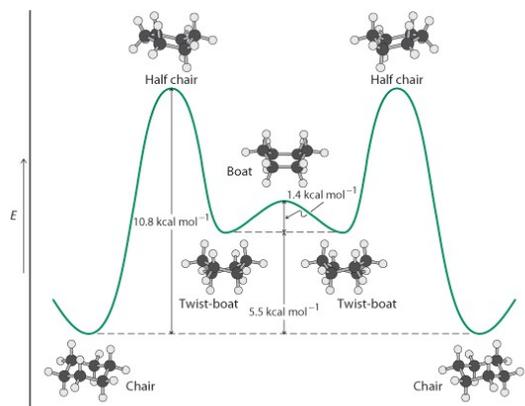
Chair flips to another chair - going through a boat

Every axial position becomes equatorial, and vice versa



Ring flipping occurs rapidly at room temperature

Energy Diagram of Energy Barrier



Flips about
100 x per sec

99.9% of
molecules in
chair form

Note: kcal/mol x 4.2 = kJ/mol

Drawing Cyclohexanes

To draw chair cyclohexanes, follow these steps:

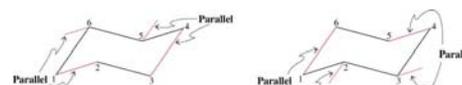
- 1.) Draw the carbon chair.
- 2.) Add the axial hydrogens.



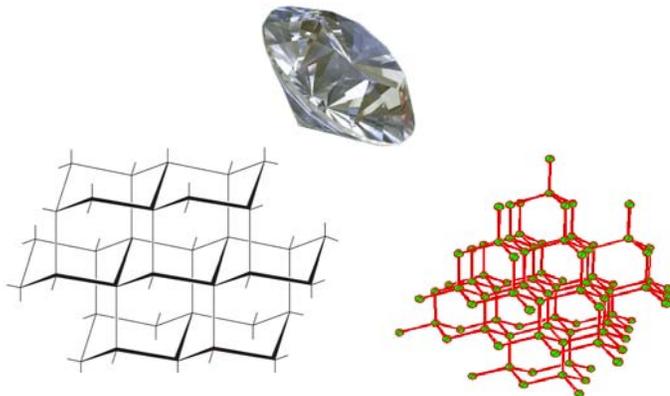
- 3.) Draw the C1 and C4 equatorial hydrogens.



- 4.) Draw the remaining equatorial hydrogens.



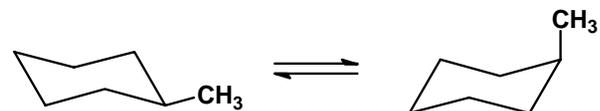
Diamond = "infinite" cyclohexane rings



Conformations of Substituted Cyclohexanes

◆ Monosubstituted Cyclohexanes

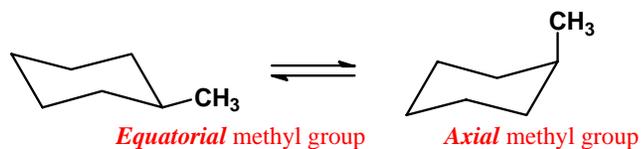
- Methylcyclohexane



Conformations of Substituted Cyclohexanes

◆ Monosubstituted Cyclohexanes

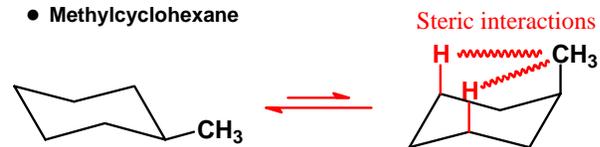
- Methylcyclohexane



Conformations of Substituted Cyclohexanes

◆ Monosubstituted Cyclohexanes

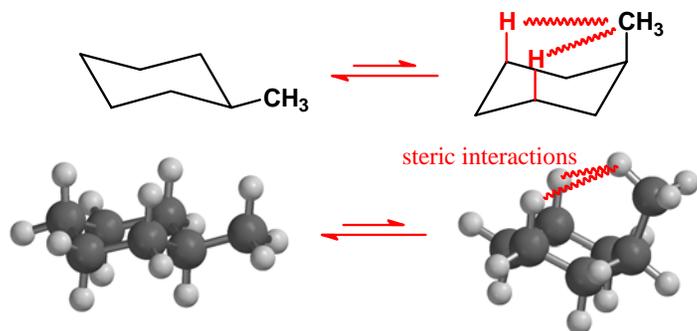
- Methylcyclohexane



Conformations of Substituted Cyclohexanes

◆ Monosubstituted Cyclohexanes

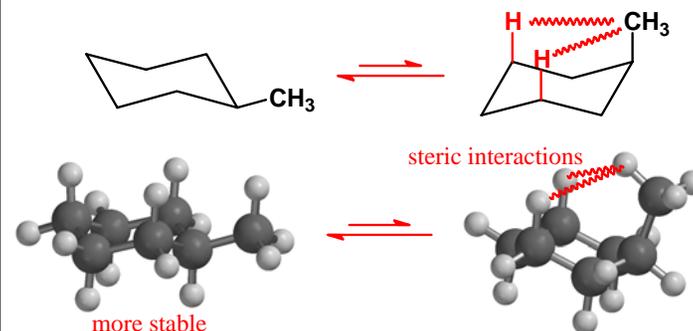
- Methylcyclohexane



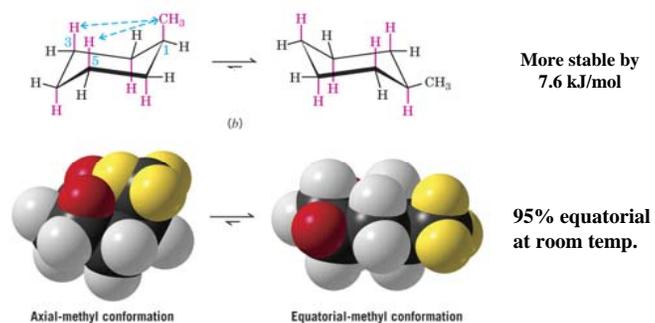
Conformations of Substituted Cyclohexanes

◆ Monosubstituted Cyclohexanes

- Methylcyclohexane

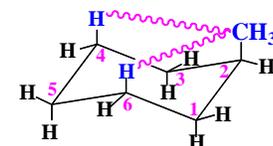


Substituted Cyclohexanes



Destabilization of axial groups due to steric interactions

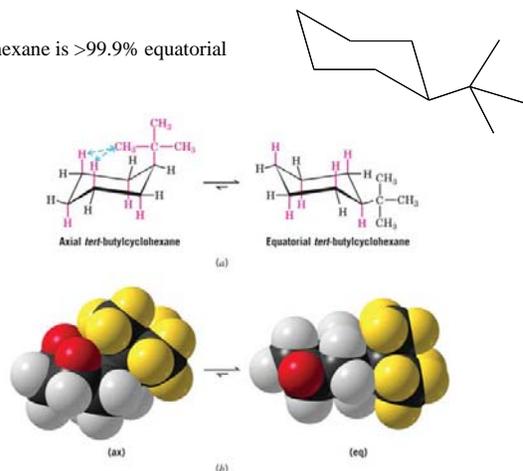
In axial methylcyclohexane there are two 1,3-diaxial interactions



Each 1,3-diaxial interaction introduces 3.75 kJ/mol of steric strain

The larger the group, the greater the equatorial preference

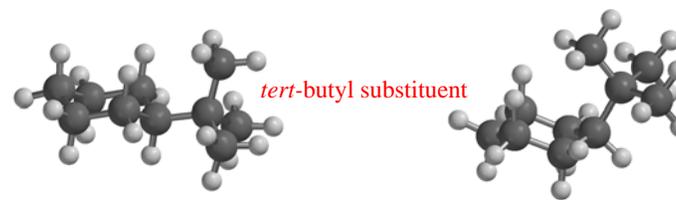
t-butylcyclohexane is >99.9% equatorial



Conformations of Substituted Cyclohexanes

◆ Monosubstituted Cyclohexanes

- tert-Butylcyclohexane



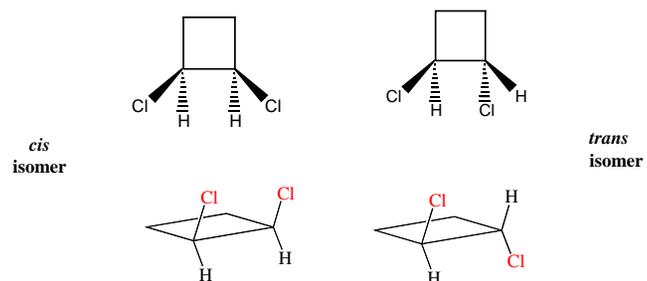
Disubstituted Cycloalkanes

With two substituents on the ring in different positions, configurational isomers arise

cis: groups on same side of ring

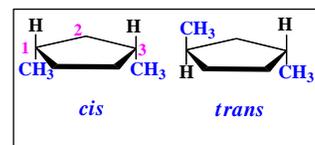
trans: groups on opposite side of ring

e.g. 1,2-Dichlorocyclobutane



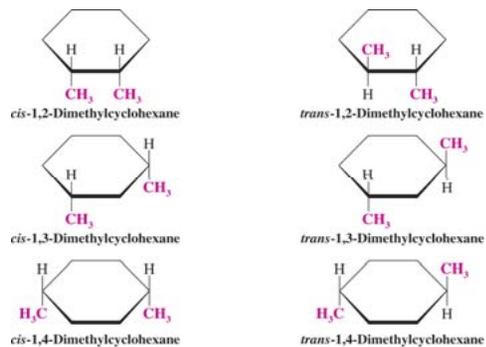
For 3, 4, or 5 membered rings, can treat as if planar

1,3-dimethylcyclopentanes



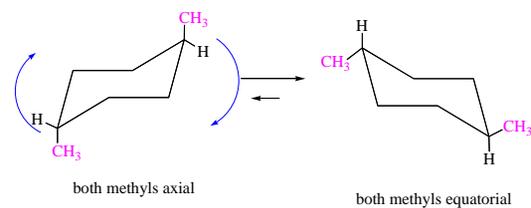
Configurational Isomers in Disubstituted Cyclohexanes

Three options for pairs of *cis-trans* cyclohexanes



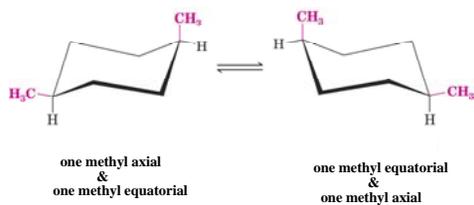
Preferred conformations

trans-1,4-Dimethylcyclohexane prefers *trans*-diequatorial conformation



Note methyls on opposite sides of ring

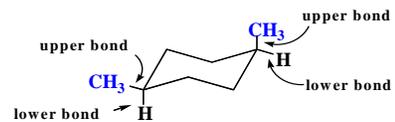
cis-1,4-Dimethylcyclohexane exists in an axial-equatorial conformation



Note that both are on the same side of ring
(top side in this drawing)

Confirming whether *cis* or *trans*

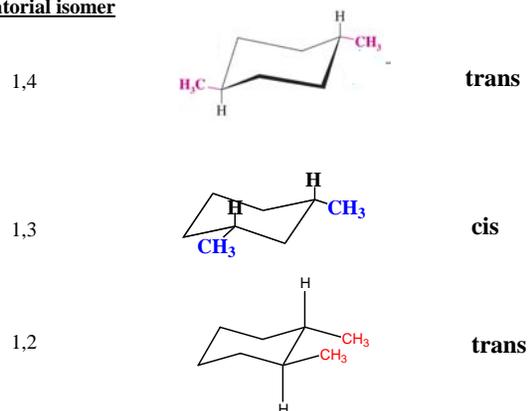
Identify each substituent as on the upper or lower side of ring



Since the two bonds to the CH_3 groups are "upper", meaning same side, they are "*cis*."

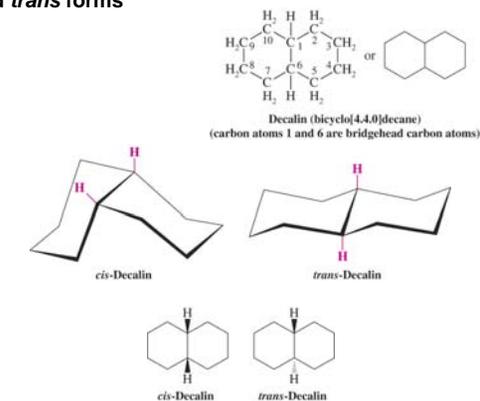
Is diequatorial always *trans*?

Di-equatorial isomer



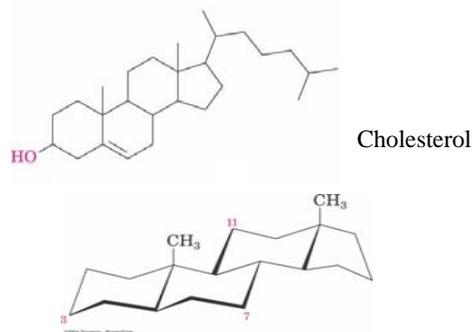
Bicyclic and Polycyclic Alkanes

The bicyclic decalin system exists in non-interconvertible *cis* and *trans* forms



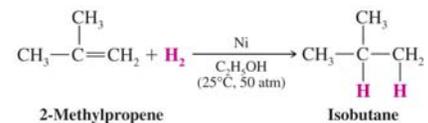
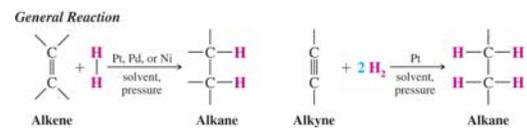
Polycyclic Alkanes

Steroid backbone



Synthesis of Alkanes and Cycloalkanes

Hydrogenation of Alkenes and Alkynes

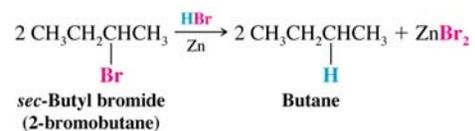


Synthesis of Alkanes and Cycloalkanes

Reduction of Alkyl Halides



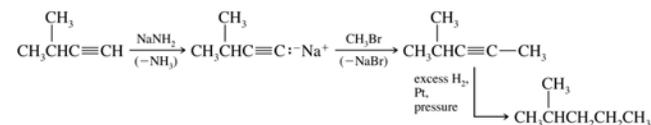
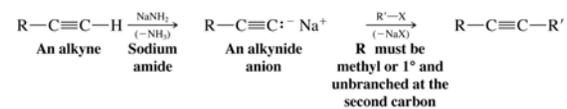
Specific Example:



Synthesis of Alkanes and Cycloalkanes

Alkylation of Terminal Alkynes

- Alkynes can be subsequently hydrogenated to alkanes



Synthesis of Alkanes and Cycloalkanes

Example: "Synthesize 2-methylpentane starting from 3-methyl-1-butyne"

