Chapter 4

Nomenclature & Conformations of Alkanes & Cycloalkanes

Created by
Professor William Tam & Dr. Phillis Chang

About The Authors

These Powerpoint Lecture Slides were created and prepared by Professor William Tam and his wife Dr. Phillis Chang.

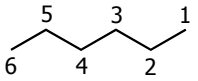
Professor William Tam received his B.Sc. at the University of Hong Kong in 1990 and his Ph.D. at the University of Toronto (Canada) in 1995. He was an NSERC postdoctoral fellow at the Imperial College (UK) and at Harvard University (USA). He joined the Department of Chemistry at the University of Guelph (Ontario, Canada) in 1998 and is currently a Full Professor and Associate Chair in the department. Professor Tam has received several awards in research and teaching, and according to *Essential Science Indicators*, he is currently ranked as the Top 1% most cited Chemists worldwide. He has published four books and over 80 scientific papers in top international journals such as *J. Am. Chem. Soc., Angew. Chem., Org. Lett.,* and *J. Org. Chem.*

Dr. Phillis Chang received her B.Sc. at New York University (USA) in 1994, her M.Sc. and Ph.D. in 1997 and 2001 at the University of Guelph (Canada). She lives in Guelph with her husband, William, and their son, Matthew.

1. Introduction to Alkanes & Cycloalkanes

- Alkanes and cycloalkanes are hydrocarbons in which all the carbon-carbon (C–C) bonds are single bonds
- Hydrocarbons that contain C=C: Alkenes
  Hydrocarbons that contain C≡C: Alkynes

- Alkanes: C_nH_{2n+2}

e.g. 

hexane (C_6H_{14})

- Cycloalkanes: C_nH_{2n}

e.g. 
cyclohexane (C_6H_{12})

1A. Sources of Alkanes: Petroleum

- Petroleum is the primary source of alkanes. It is a complex mixture of mostly alkanes and aromatic hydrocarbons with small amounts of oxygen-, nitrogen-, and sulfur-containing compounds

- Petroleum refining
  - Distillation is the first step in refining petroleum. Its components are separated based on different volatility
  - More than 500 different compounds are contained in petroleum distillates boiling below 200°C

❖ Petroleum refining (Cont'd)

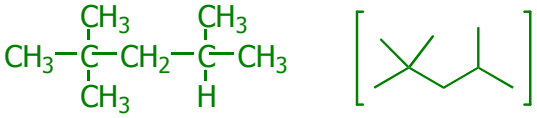
- The fractions taken contain a mixture of alkanes of similar boiling points
- Mixture of alkanes can be used as fuels, solvents, and lubricants

❖ Gasoline

- The demand of gasoline is much greater than that supplied by the gasoline fraction of petroleum
- Converting hydrocarbons from other fractions of petroleum into gasoline by "*catalytic cracking*"

mixture of alkanes (C_{12} and higher) $\xrightarrow[\sim 500^{\circ}C]{\text{catalysts}}$ highly branched hydrocarbons (C_5 - C_{10})

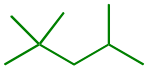
❖ Gasoline (Cont'd)



2,2,4-Trimethylpentane (isooctane)
($C_{12}H_{18}$)

- Isooctane burns very smoothly (without knocking) in internal combustion engines and is used as one of the standards by which the octane rating of gasoline is established

❖ Gasoline (Cont'd)



isooctane

heptane

"octane rating"	100	0

- e.g. a gasoline of a mixture: 87% isooctane and 13% heptane
  - ♦ Rated as 87-octane gasoline

Typical Fractions Obtained by Distillation of Petroleum

Boiling Range of Fraction (°C)	# of Carbon Atoms per Molecule	Use
Below 20	C_1 – C_4	Natural gas, bottled gas, petrochemicals
20 – 60	C_5 – C_6	Petroleum ether, solvents
60 – 100	C_6 – C_7	Ligroin, solvents
40 – 200	C_5 – C_{10}	Gasoline (straight-run gasoline)
175 – 325	C_{12} – C_{18}	Kerosene and jet fuel

Typical Fractions Obtained by Distillation of Petroleum (Cont'd)

Boiling Range of Fraction (°C)	# of Carbon Atoms per Molecule	Use
250 – 400	C_{12} and higher	Gas oil, fuel oil, and diesel oil
Nonvolatile liquids	C_{20} and higher	Refined mineral oil, lubricating oil, and grease
Nonvolatile solids	C_{20} and higher	Paraffin wax, asphalt, and tar

2. Shapes of Alkanes

- All carbon atoms in alkanes and cycloalkanes are sp^3 hybridized, and they all have a **tetrahedral** geometry
- Even "straight-chain" alkanes are not straight. They have a zigzag geometry

- "Straight-chain" (unbranched) alkanes

Butane

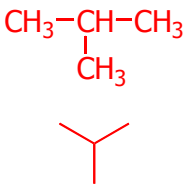
$CH_3CH_2CH_2CH_3$

Pentane

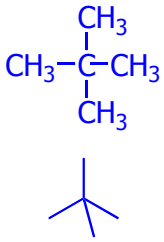
$CH_3CH_2CH_2CH_2CH_3$

- Branched-chain alkanes

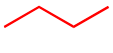
Isobutane



Neopentane



- Butane and isobutane have the same molecular formula (C_4H_{10}) but different bond connectivities. Such compounds are called constitutional isomers



Butane

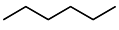
Isobutane

- C_4 and higher alkanes exist as constitutional isomers. The number of constitutional isomers increases rapidly with the carbon number

Molecular Formula	# of Possible Const. Isomers	Molecular Formula	# of Possible Const. Isomers
C_4H_{10}	2	C_9H_{20}	35
C_5H_{12}	3	$C_{10}H_{22}$	75
C_6H_{14}	5	$C_{20}H_{42}$	366,319
C_7H_{16}	9	$C_{40}H_{82}$	62,481,801,147,341
C_8H_{18}	18		

- Constitutional isomers usually have different physical properties

Hexane Isomers (C_6H_{14})

Formula	M.P. (°C)	B.P. (°C)	Density (g/mL)	Refractive Index
	-95	68.7	0.6594	1.3748
	-153.7	60.3	0.6532	1.3714
	-118	63.3	0.6643	1.3765
	-128.8	58	0.6616	1.3750
	-98	49.7	0.6492	1.3688

3. IUPAC Nomenclature of Alkanes, Alkyl Halides, & Alcohols

- One of the most commonly used nomenclature systems that we use today is based on the system and rules developed by the *International Union of Pure and Applied Chemistry (IUPAC)*
- Fundamental Principle: Each different compound shall have a unique name

- Although the IUPAC naming system is now widely accepted among chemists, common names (trivial names) of some compounds are still widely used by chemists and in commerce. Thus, learning some of the common names of frequently used chemicals and compounds is still important

- The ending for all the names of alkanes is *–ane*
- The names of most alkanes stem from Greek and Latin

one two three four five

meth- eth- prop- but- pent-

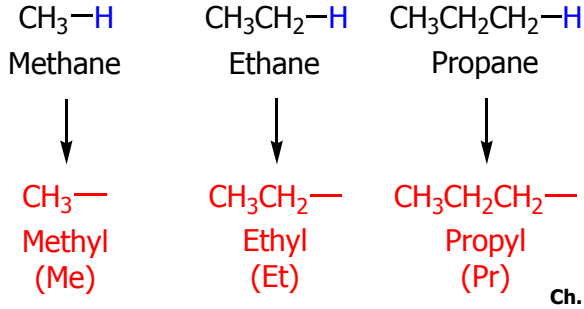
- Unbranched alkanes

Name	***Structure***	***Name***	***Structure***
Methane	CH_4	Hexane	$CH_3(CH_2)_4CH_3$
Ethane	CH_3CH_3	Heptane	$CH_3(CH_2)_5CH_3$
Propane	$CH_3CH_2CH_3$	Octane	$CH_3(CH_2)_6CH_3$
Butane	$CH_3CH_2CH_2CH_3$	Nonane	$CH_3(CH_2)_7CH_3$
Pentane	$CH_3(CH_2)_3CH_3$	Decane	$CH_3(CH_2)_8CH_3$

3A. Nomenclature of Unbranched Alkyl Groups

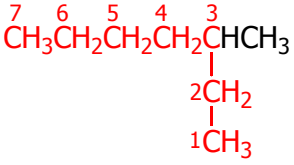
- Alkyl group
  - Removal of one hydrogen atom from an alkane

- Alkyl group (Cont'd)
  - For an unbranched alkane, the hydrogen atom that is removed is a terminal hydrogen atom

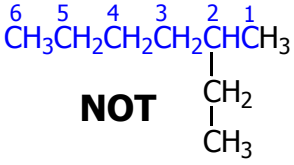


3B. Nomenclature of Branched-Chain Alkanes

- Rule
  1. Use the longest continuous carbon chain as parent name



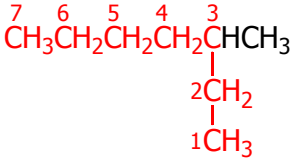
(3-Methylheptane)



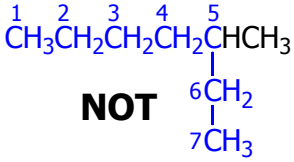
NOT

(2-Ethylhexane)

- Rule (Cont'd)
  2. Use the lowest number of the substituent
  3. Use the number obtained by Rule 2 to designate the location of the substituent



(3-Methylheptane)

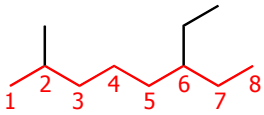


NOT

(5-Methylheptane)

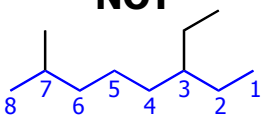
- Rule (Cont'd)
  4. For two or more substituents, use the lowest possible individual numbers of the parent chain
     The substitutents should be listed alphabetically. In deciding alphabetical order, disregard multiplying prefix, such as "di", "tri" etc.

- Rule (Cont'd)



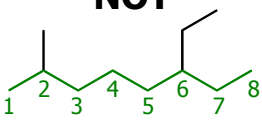
(6-Ethyl-2-methyloctane)

NOT



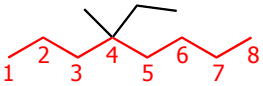
(3-Ethyl-7-methyloctane)

NOT



(2-Methyl-6-ethyloctane)

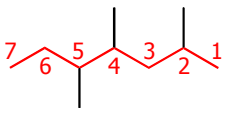
- Rule (Cont'd)
  5. When two substituents are present on the same carbon, use that number twice



(4-Ethyl-4-methyloctane)

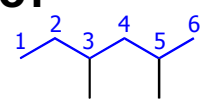
- Rule (Cont'd)
  6. For identical substituents, use prefixes di-, tri-, tetra- and so on

(2,4-Dimethylhexane)



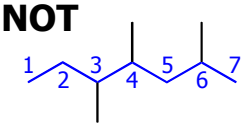
(2,4,5-Trimethylheptane)

NOT



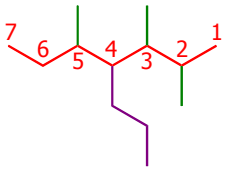
(3,5-Dimethylhexane)

NOT

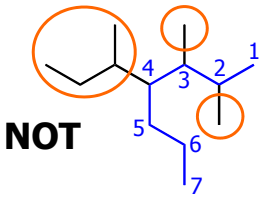


(3,4,6-Trimethylheptane)

- Rule (Cont'd)
  7. When two chains of equal length compete for selection as parent chain, choose the chain with the greater number of substituents

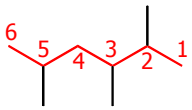


(2,3,5-Trimethyl-4-propylheptane)

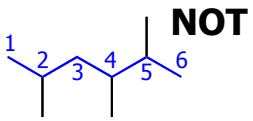


(only three substituents)

- Rule (Cont'd)
  8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference

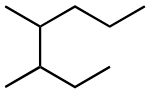


(2,3,5-Trimethylhexane)

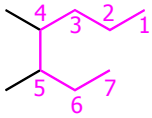


(2,4,5-Trimethylhexane)

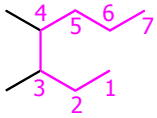
- Example 1



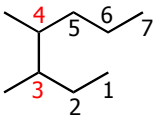
  - Find the longest chain as parent



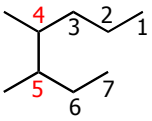
or



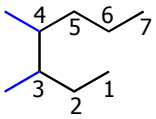
- Example 1 (Cont'd)
  - Use the lowest numbering for substituents



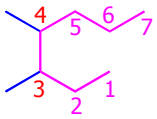
instead of



  - Substituents: two methyl groups
    - dimethyl

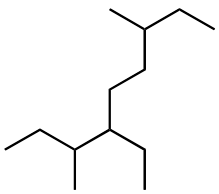


- Example 1 (Cont'd)
  - Complete name

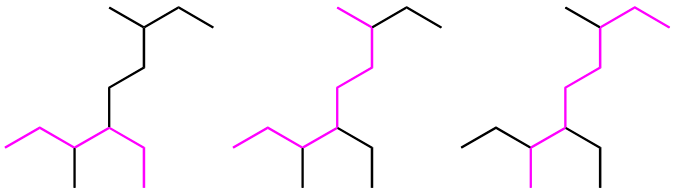


(3,4-Dimethylheptane)

- Example 2

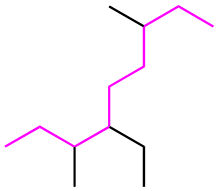


- Example 2 (Cont'd)
  - Find the longest chain as parent



6-carbon chain 8-carbon chain 8-carbon chain

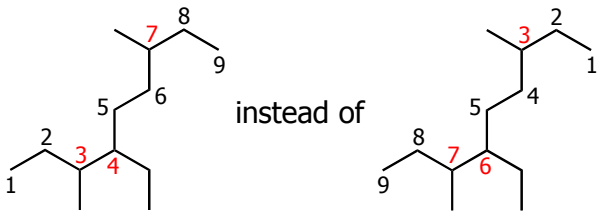
- Example 2 (Cont'd)
  - Find the longest chain as parent



9-carbon chain
(correct!)

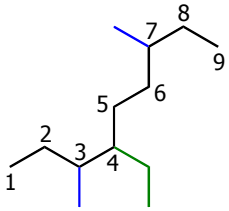
⇒ Nonane as parent

- Example 2 (Cont'd)
  - Use the lowest numbering for substituents

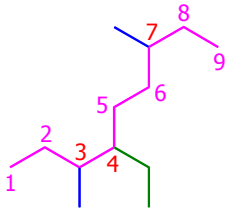


(3,4,7) (3,6,7)

- Example 2 (Cont'd)
  - Substituents
    - 3,7-dimethyl
    - 4-ethyl



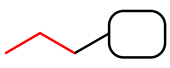
- Example 2 (Cont'd)
  - Substituents in alphabetical order
    - Ethyl before dimethyl
      (recall Rule 4 – disregard "di")
  - Complete name



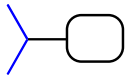
(4-Ethyl-3,7-dimethylnonane)

3C. Nomenclature of Branched Alkyl Groups

- For alkanes with more than two carbon atoms, more than one derived alkyl group is possible
- Three-carbon groups

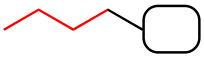


Propyl

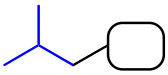


Isopropyl
(or 1-methylethyl)

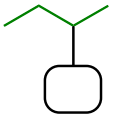
❖ Four-carbon groups



Butyl



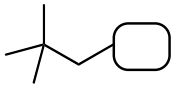
Isobutyl



sec-butyl
(1-methylpropyl)

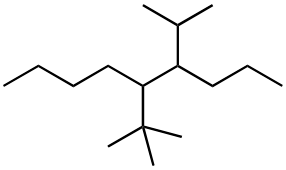
tert-butyl
(or 1,1-dimethylethyl)

❖ A neopentyl group



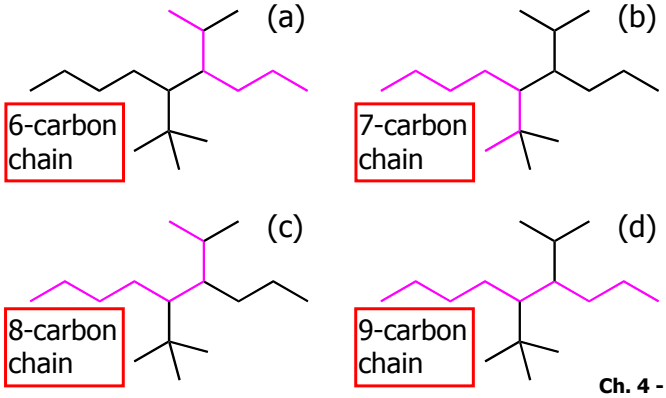
neopentyl
(2,2,-dimethylpropyl)

❖ Example 1



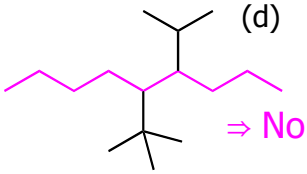
❖ Example 1 (Cont'd)

- Find the longest chain as parent

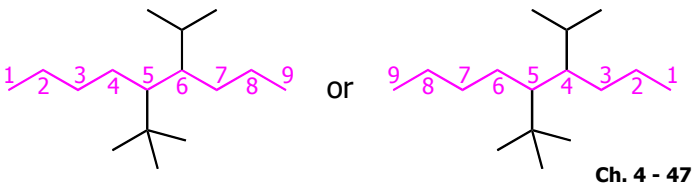


❖ Example 1 (Cont'd)

- Find the longest chain as parent

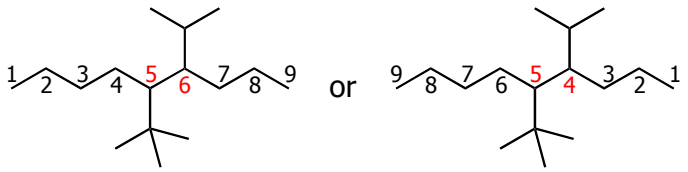


⇒ Nonane as parent



❖ Example 1 (Cont'd)

- Use the lowest numbering for substituents



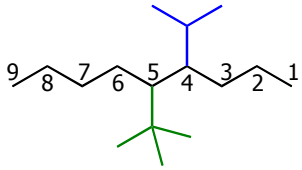
5,6

4,5
(lower numbering)

⇒ Use 4,5

❖ Example 1 (Cont'd)

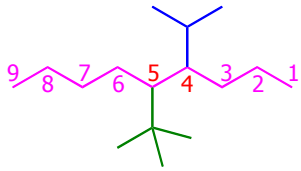
- Substituents
  - ♦ Isopropyl
  - ♦ *tert*-butyl



⇒ 4-isopropyl and 5-*tert*-butyl

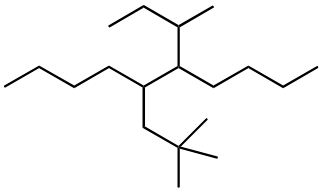
❖ Example 1 (Cont'd)

- Alphabetical order of substituents
  - ♦ *tert*-butyl before isopropyl
- Complete name



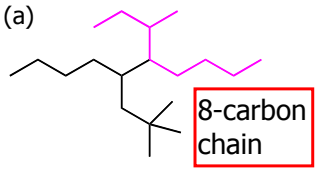
5-*tert*-Butyl-4-isopropylnonane

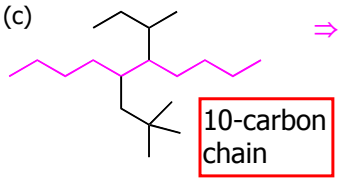
❖ Example 2



❖ Example 2 (Cont'd)

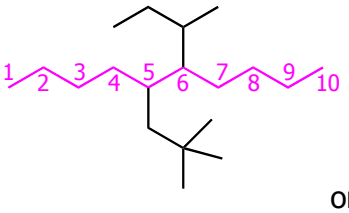
- Find the longest chain as parent



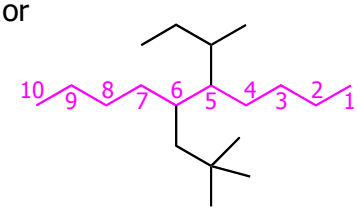


⇒ Octane as parent

❖ Example 2 (Cont'd)

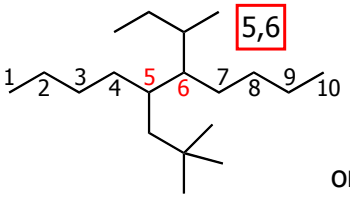


or

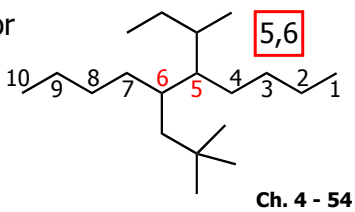


❖ Example 2 (Cont'd)

- Use the lowest numbering for substituents



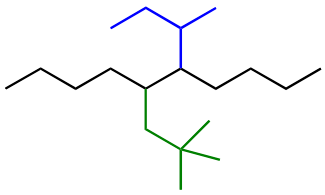
or



⇒ Determined using the next Rules

❖ Example 2 (Cont'd)

- Substituents
  - ♦ *sec*-butyl
  - ♦ Neopentyl

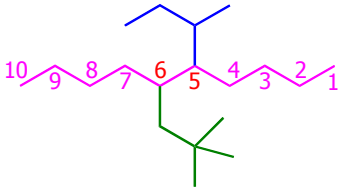


But is it
- 5-*sec*-butyl and 6-neopentyl or
- 5-neopentyl and 6-*sec*-butyl ?

❖ Example 2 (Cont'd)

- Since *sec*-butyl takes precedence over neopentyl
  - ♦ 5-*sec*-butyl and 6-neopentyl

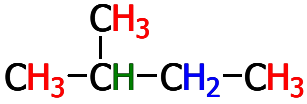
- Complete name



5-*sec*-Butyl-6-neopentyldecane

3D. Classification of Hydrogen Atoms

1° hydrogen atoms



3° hydrogen atoms 2° hydrogen atoms

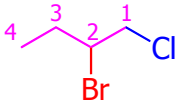
3E. Nomenclature of Alkyl Halides

❖ Rules

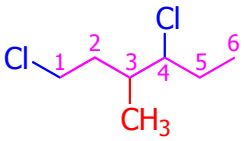
- Halogens are treated as substituents (as prefix)
  F: fluoro Br: bromo
  Cl: chloro I: iodo

- Similar rules as alkyl substituents

❖ Examples



2-Bromo-1-chlorobutane

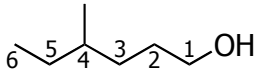


1,4-Dichloro-3-methylhexane

3F. Nomenclature of Alcohols

❖ IUPAC substitutive nomenclature: a name may have as many as four features

- Locants, prefixes, parent compound, and suffixes

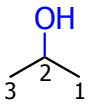


4-Methyl-1-hexanol

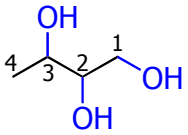
❖ Rules

- Select the longest continuous carbon chain to which the hydroxyl is directly attached. Change the name of the alkane corresponding to this chain by dropping the final ***–e*** and adding the suffix ***–ol***
- Number the longest continuous carbon chain so as to give the carbon atom bearing the hydroxyl group the lower number. Indicate the position of the hydroxyl group by using this number as a locant

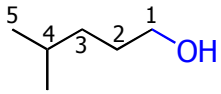
❖ Examples



2-Propanol
(isopropyl alcohol)

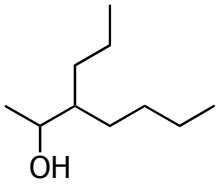


1,2,3-Butanetriol



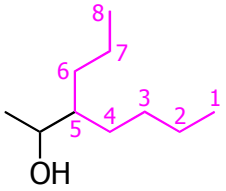
4-Methyl-1-pentanol
(or 4-Methylpentan-1-ol)
(**NOT** 2-Methyl-5-pentanol)

❖ Example 4

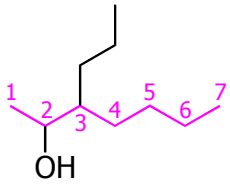


❖ Example 4 (Cont'd)

- Find the longest chain as parent



or



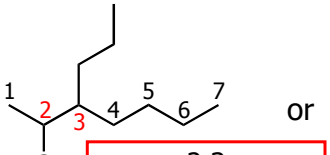
Longest chain but does not contain the OH group

7-carbon chain containing the OH group

⇒ Heptane as parent

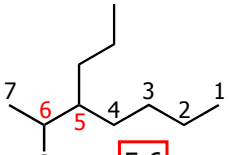
❖ Example 4 (Cont'd)

- Use the lowest numbering for the carbon bearing the OH group



2,3
(lower numbering)

or

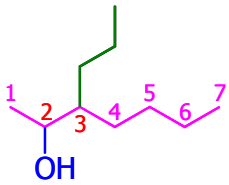


5,6

⇒ Use 2,3

❖ Example 4 (Cont'd)

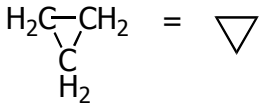
- Parent and suffix
  - ♦ 2-Heptanol
- Substituents
  - ♦ Propyl
- Complete name
  - ♦ 3-Propyl-2-heptanol



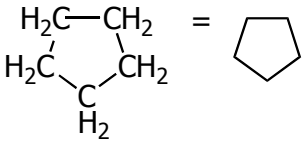
4. How to Name Cycloalkanes

4A. Monocyclic Compounds

- Cycloalkanes with only one ring
  - Attach the prefix ***cyclo-***

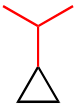


Cyclopropane



Cyclopentane

- Substituted cycloalkanes

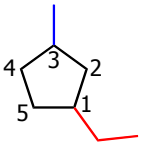


Isopropylcyclopropane

Methylcyclopropane

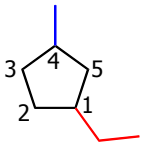
tert-Butylcyclopentane

- Example 1



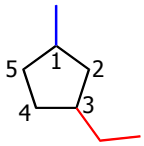
1-Ethyl-3-methyl-cyclopentane

NOT



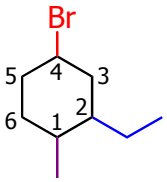
1-Ethyl-4-methyl-cyclopentane

NOT



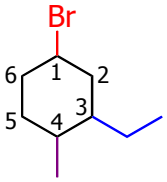
3-Ethyl-1-methyl-cyclopentane

- Example 2



4-Bromo-2-ethyl-1-methyl cyclohexane

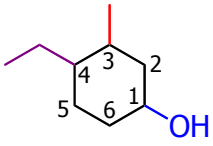
NOT



1-Bromo-3-ethyl-4-methyl cyclohexane

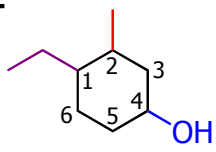
(lowest numbers of substituents are 1,2,4 not 1,3,4)

- Example 3



4-Ethyl-3-methyl cyclohexanol

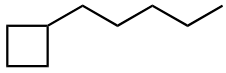
NOT



1-Ethyl-2-methyl cyclohexan-4-ol

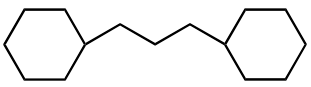
(the carbon bearing the OH should have the lowest numbering, even though 1,2,4 is lower than 1,3,4)

- Cycloalkylalkanes
  - When a single ring system is attached to a single chain with a greater number of carbon atoms



1-Cyclobutylpentane

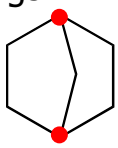
  - When more than one ring system is attached to a single chain



1,3-Dicyclohexylpropane

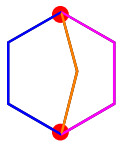
4B. Bicyclic Compounds

- Bicycloalkanes
  - Alkanes containing two fused or bridged rings



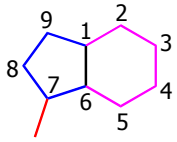
  - Total # of carbons = 7
    - Bicycloheptane
  - Bridgehead

- Example (Cont'd)

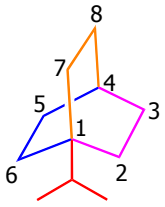


- Between the two bridgeheads
  - Two-carbon bridge on the left
  - Two-carbon bridge on the right
  - One-carbon bridge in the middle
- Complete name
  - Bicyclo[2.2.1]heptane

- Other examples



7-Methylbicyclo[4.3.0]nonane



1-Isopropylbicyclo[2.2.2]octane

5. Nomenclature of Alkenes & Cycloalkenes

- Rule
  1. Select the longest chain that contains C=C as the parent name and change the name ending of the alkane of identical length from ***–ane*** to ***–ene***

- Rule
  2. Number the chain so as to include both carbon atoms of C=C, and begin numbering at the end of the chain nearer C=C. Assign the location of C=C by using the number of the first atom of C=C as the prefix. The locant for the alkene suffix may precede the parent name or be placed immediately before the suffix

- Examples

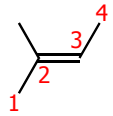
$\overset{1}{CH_2}=\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$

1-Butene
(not 3-Butene)

$\overset{1}{C}H_3\overset{2}{C}H=\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$

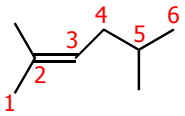
2-Hexene
(not 4-Hexene)

- Rule
  3. Indicate the locations of the substituent groups by the numbers of the carbon atoms to which they are attached
  - Examples



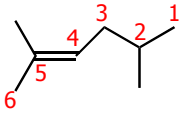
2-Methyl-2-butene
(not 3-Methyl-2-butene)

- Examples (Cont'd)



2,5-Dimethyl-2-hexene

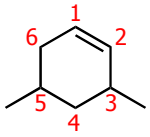
NOT



2,5-Dimethyl-4-hexene

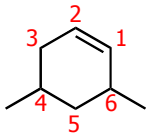
- Rule
  4. Number substituted cycloalkenes in the way that gives the carbon atoms of C=C the 1 and 2 positions and that also gives the substituent groups the lower numbers at the first point of difference

- Example



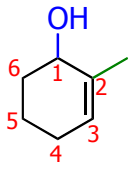
3,5-Dimethylcyclohexene

NOT



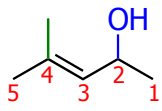
4,6-Dimethylcyclohexene

- Rule
  5. Name compounds containing a C=C and an alcohol group as alkenols (or cycloalkenols) and give the alcohol carbon the lower number
  - Examples



2-Methyl-2-cyclohexen-1-ol
(or 2-Methylcyclohex-2-en-1-ol)

- Examples (Cont'd)



4-Methyl-3-penten-2-ol
(or 4-Methylpent-3-en-2-ol)

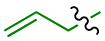
- Rule
  6. Vinyl group & allyl group

Vinyl group

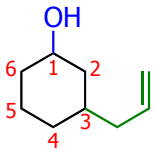
ethenyl

Ethenylcyclopropane
(or Vinylcyclopropane)

Allyl group

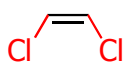


prop-2-en-1-yl

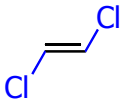


3-(Prop-2-en-1-yl)
cyclohexan-1-ol
(or 3-Allylcyclohexanol)

- Rule
  7. Cis vs. Trans
     - *Cis:* two identical or substantial groups on the same side of C=C
     - *Trans:* two identical or substantial groups on the opposite side of C=C

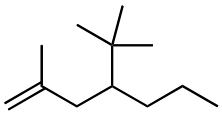


cis-1,2-Dichloroethene



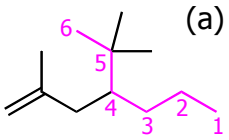
trans-1,2-Dichloroethene

- Example

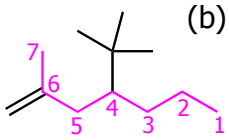


- Example (Cont'd)

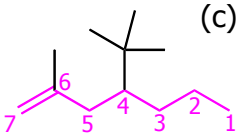
(a)



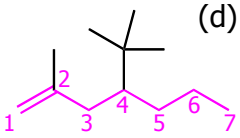
(b)



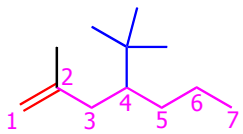
(c)



(d)



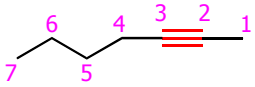
- Example (Cont'd)
  - Complete name



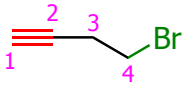
4-*tert*-Butyl-2-methyl-1-heptene

6. Nomenclature of Alkynes

- Alkynes are named in much the same way as alkenes, but ending name with ***–yne*** instead of ***–ene***
- Examples

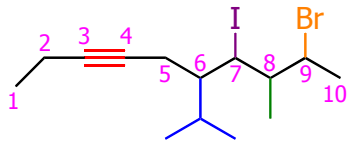


2-Heptyne



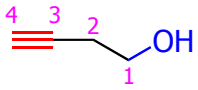
4-Bromo-1-butyne

- Examples (Cont'd)

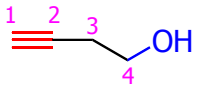


9-Bromo-7-iodo-6-isopropyl-8-methyl-3-decyne

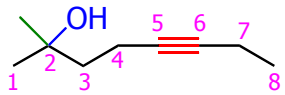
- OH group has priority over C≡C



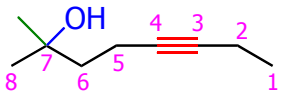
NOT



3-Butyn-1-ol



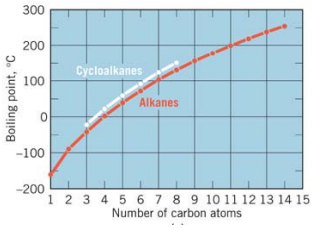
2-Methyl-5-octyn-2-ol

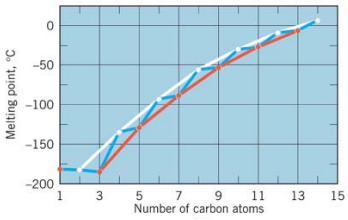


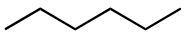
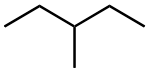
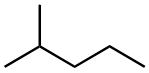
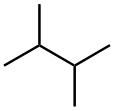
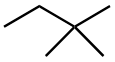
NOT

7. Physical Properties of Alkanes & Cycloalkanes

- Boiling points & melting points





C_6H_{14} Isomer	Boiling Point (°C)
	68.7
	63.3
	60.3
	58
	49.7

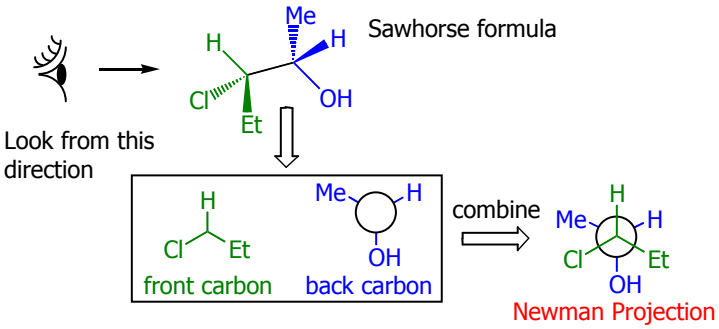
Physical Constants of Cycloalkanes

# of C Atoms	*Name*	*bp (°C)*	*mp (°C)*	*Density*	*Refractive Index*
3	Cyclopropane	-33	-126.6	-	-
4	Cyclobutane	13	-90	-	1.4260
5	Cyclopentane	49	-94	0.751	1.4064
6	Cyclohexane	81	6.5	0.779	1.4266
7	Cycloheptane	118.5	-12	0.811	1.4449
8	Cyclooctane	149	13.5	0.834	-

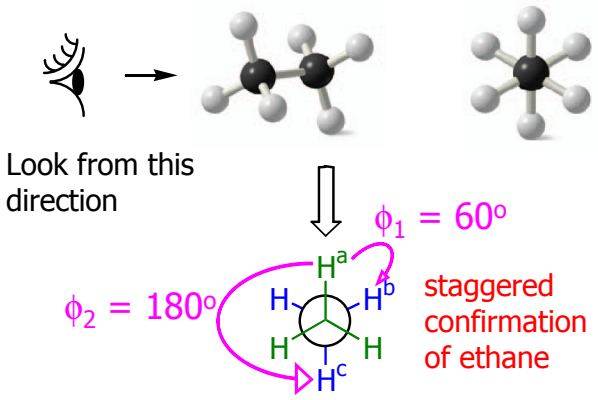
8. Sigma Bonds & Bond Rotation

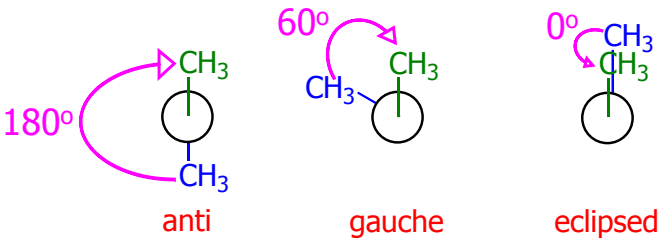
- Two groups bonded by a single bond can undergo rotation about that bond with respect to each other
  - **Conformations** – temporary molecular shapes result from a rotation about a single bond
  - **Conformer** – each possible structure of conformation
  - **Conformational analysis** – analysis of energy changes occur as a molecule undergoes rotations about single bonds

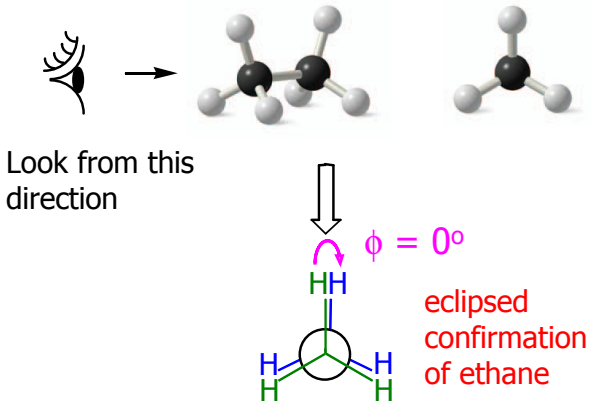
8A. Newman Projections

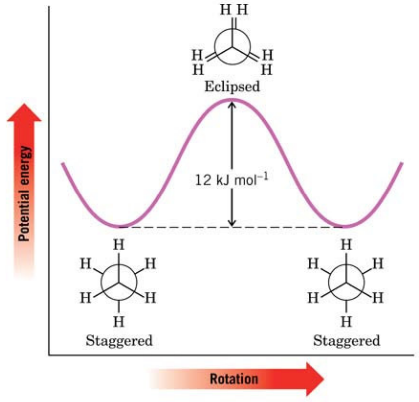


8B. How to Do a Conformational Analysis

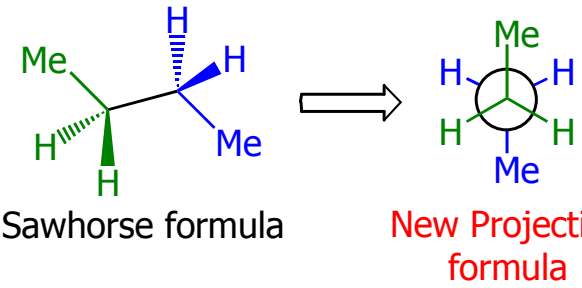


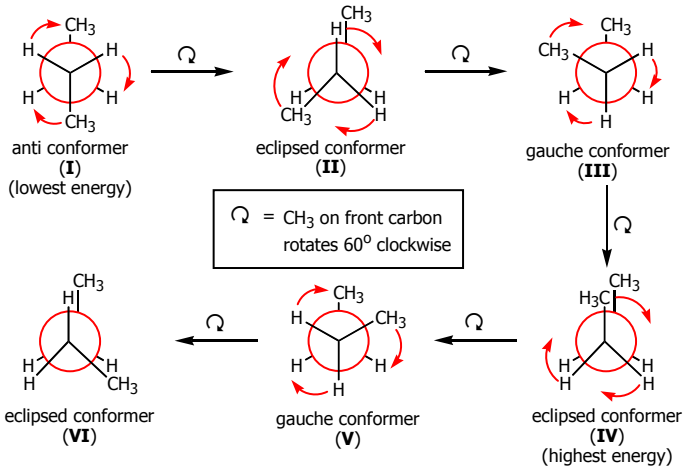


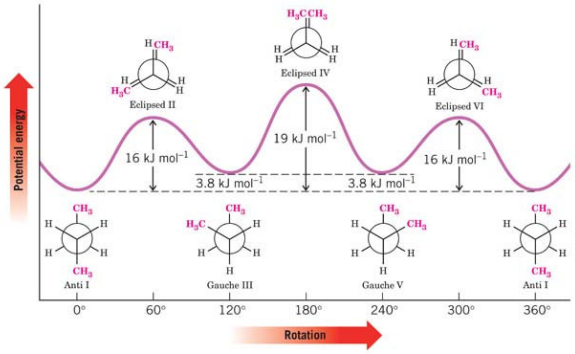




9. Conformational Analysis of Butane



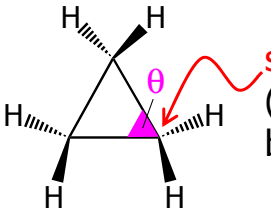




10. The Relative Stabilities of Cycloalkanes: Ring Strain

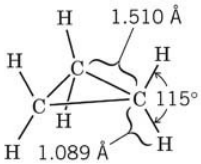
- Cycloalkanes do not have the same relative stability due to ring strain
- Ring strain comprises:
  - Angle strain – result of deviation from ideal bond angles caused by inherent structural constraints
  - Torsional strain – result of dispersion forces that cannot be relieved due to restricted conformational mobility

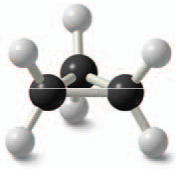
10A. Cyclopropane



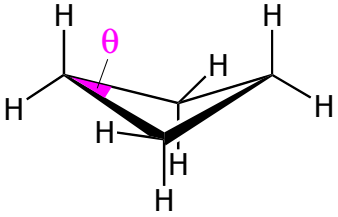
sp^3 hybridized carbon (normal tetrahedral bond angle is 109.5°)

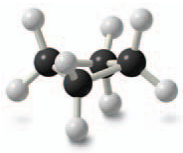
- Internal bond angle (θ) ~60° (~49.5° deviated from the ideal tetrahedral angle)





10B. Cyclobutane

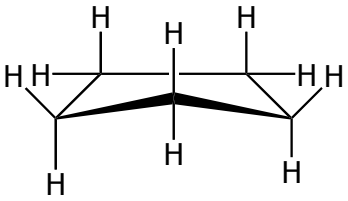


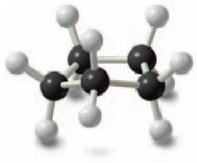


- Internal bond angle (θ) ~88° (~21° deviated from the normal 109.5° tetrahedral angle)

- Cyclobutane ring is not planar but is slightly folded.
- If cyclobutane ring were planar, the angle strain would be somewhat less (the internal angles would be 90° instead of 88°), but torsional strain would be considerably larger because all eight C–H bonds would be eclipsed

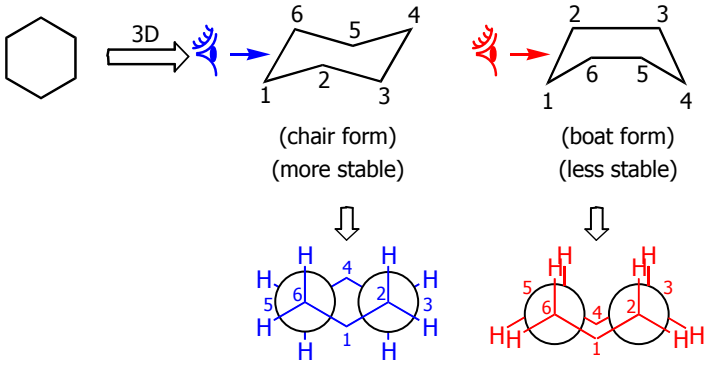
10C. Cyclopentane



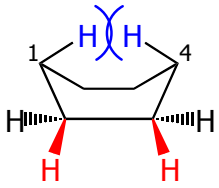


- If cyclopentane were planar, θ ~108°, very close to the normal tetrahedral angle of 109.5°
- However, planarity would introduce considerable torsional strain (i.e. 10 C–H bonds eclipsed)
- Therefore cyclopentane has a slightly bent conformation

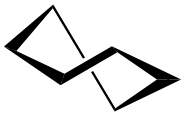
11. Conformations of Cyclohexane: The Chair & the Boat



- The boat conformer of cyclohexane is less stable (higher energy) than the chair form due to
  - Eclipsed conformation
  - 1,4-flagpole interactions



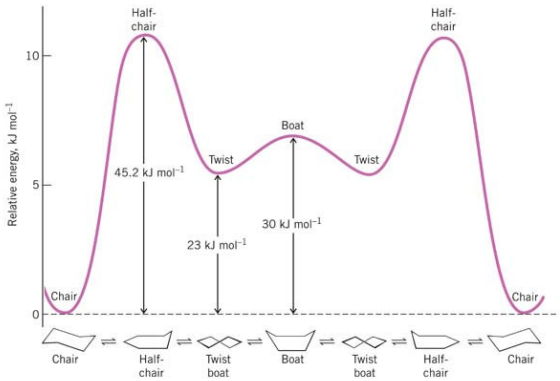
(eclipsed)



(twist boat)

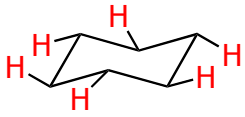
- The twist boat conformation has a lower energy than the pure boat conformation, but is not as stable as the chair conformation

- Energy diagram

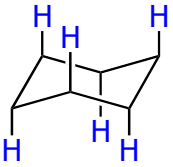


12. Substituted Cyclohexanes: Axial & Equatorial Hydrogen Atoms

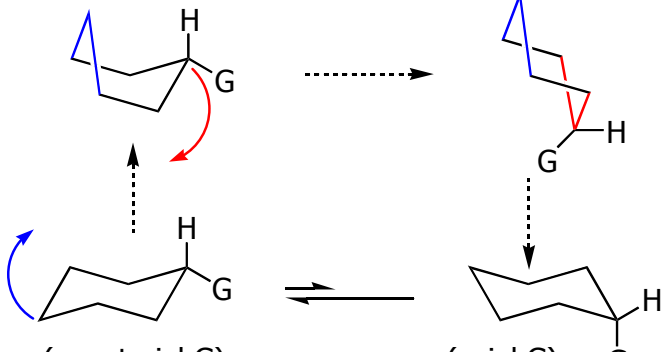
- Equatorial hydrogen atoms in chair form



- Axial hydrogen atoms in chair form



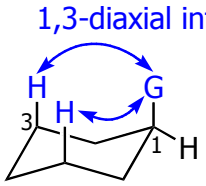
- Substituted cyclohexane
  - Two different chair forms



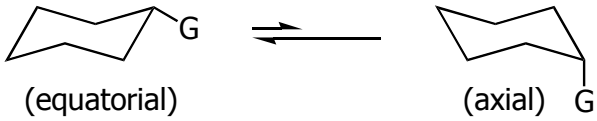
(equatorial G)
(more stable)

(axial G)
(less stable)

- The chair conformation with axial G is less stable due to 1,3-diaxial interaction



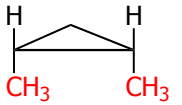
- The larger the G group, the more severe the 1,3-diaxial interaction and shifting the equilibrium from the axial-G chair form to the equatorial-G chair form



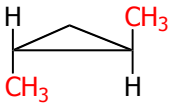
(equatorial) (axial)

At 25°C		
G	% of Equatorial	% of Axial
F	60	40
CH_3	95	5
^{i}Pr	97	3
^{t}Bu	> 99.99	< 0.01

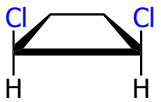
13. Disubstituted Cycloalkanes Cis-Trans Isomerism



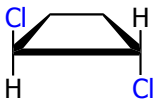
cis-1,2-Dimethyl cyclopropane



trans-1,2-Dimethyl cyclopropane



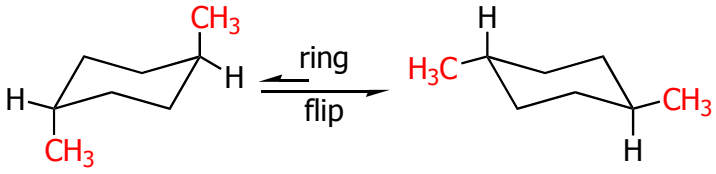
cis-1,2-Dichloro cyclobutane



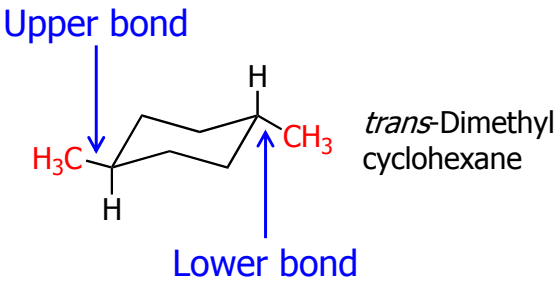
trans-1,2-Dichloro cyclobutane

13A. Cis-Trans Isomerism & Conformation Structures of Cyclohexanes

- *Trans*-1,4-Disubstituted Cyclohexanes



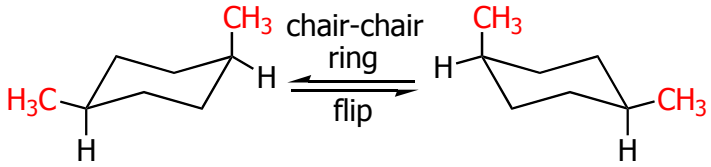
trans-Diaxial *trans*-Diequatorial



trans-Dimethyl cyclohexane

- Upper-lower bonds means the groups are *trans*

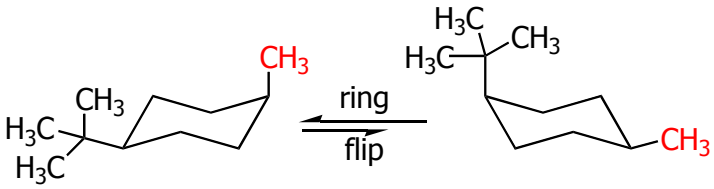
- *Cis*-1,4-Disubstituted Cyclohexanes



Equatorial-axial

Axial-equatorial

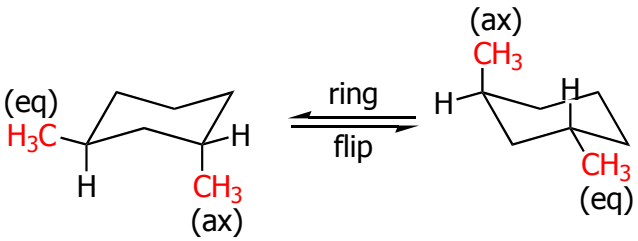
- *Cis*-1-*tert*-Butyl-4-methylcyclohexane



(more stable because large group is equatorial)

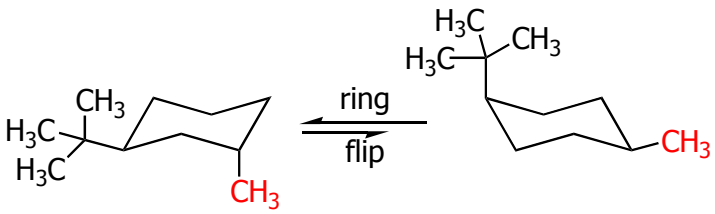
(less stable because large group is axial)

- *Trans*-1,3-Disubstituted Cyclohexanes



trans-1,3-Dimethylcyclohexane

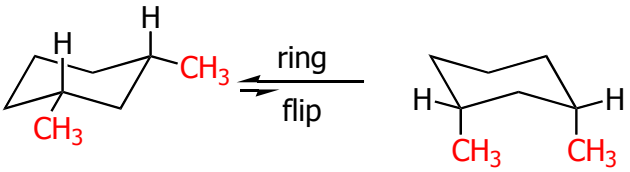
- *Trans*-1-*tert*-Butyl-3-methylcyclohexane



(more stable because large group is equatorial)

(less stable because large group is axial)

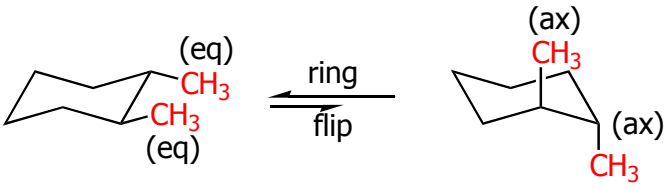
- *Cis*-1,3-Disubstituted Cyclohexanes



(more stable)

(less stable)

❖ *Trans*-1,2-Disubstituted Cyclohexanes

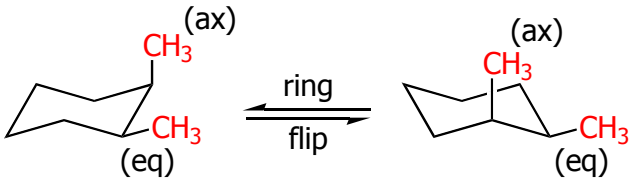


diequatorial
(much more stable)

diaxial
(much less stable)

trans-1,2-Dimethylcyclohexane

❖ *Cis*-1,2-Disubstituted Cyclohexane

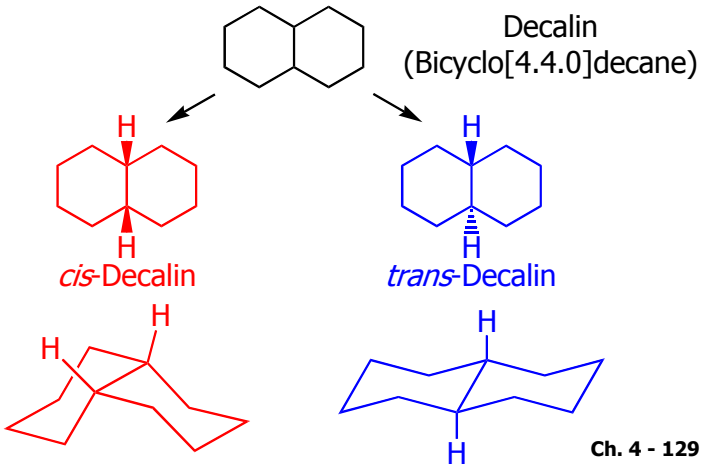


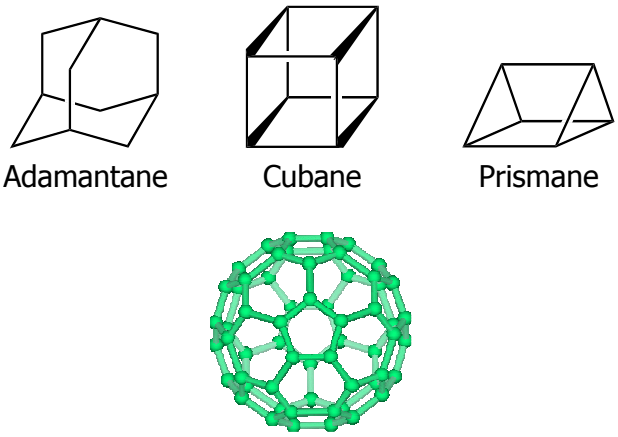
(equatorial-axial)

(axial-equatorial)

cis-1,2-Dimethylcyclohexane
(equal energy and equally populated conformations)

14. Bicyclic & Polycyclic Alkanes





Adamantane

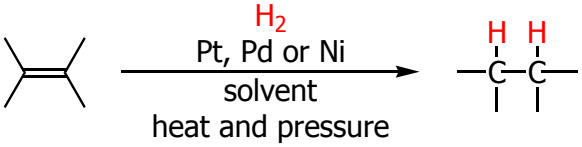
Cubane

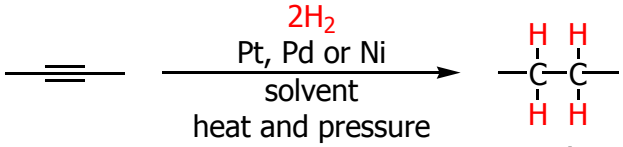
Prismane

C_{60} (Buckminsterfullerene)

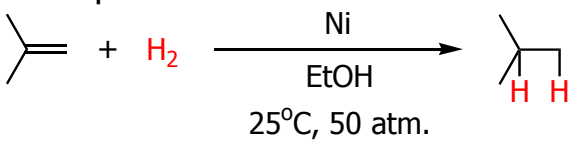
16. Synthesis of Alkanes and Cycloalkanes

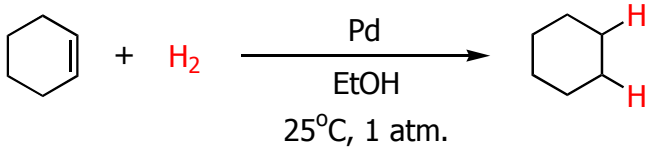
16A. Hydrogenation of Alkenes & Alkynes

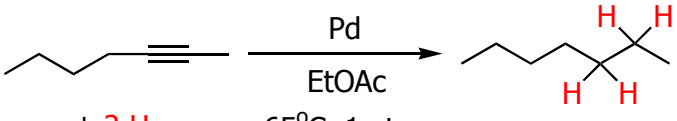




❖ Examples





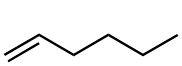


17. How to Gain Structural Information from Molecular Formulas & Index of Hydrogen Deficiency

- Index of hydrogen deficiency (IHD)
  - The difference in the number of pairs of hydrogen atoms between the compound under study and an acyclic alkane having the same number of carbons
  - Also known as "degree of unsaturation" or "double-bond equivalence" (DBE)

- Index of hydrogen deficiency (Cont'd)
  - Saturated acyclic alkanes: C_nH_{2n+2}
  - Each double bond on ring: 2 hydrogens less
  - Each double bond on ring provides one unit of hydrogen deficiency

- e.g.  Hexane: C_6H_{14}

 and  C_6H_{12}

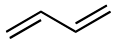
1-Hexene Cycloheane

Index of hydrogen deficiency (IHD) = $\frac{C_6H_{14} - C_6H_{12}}{H_2}$

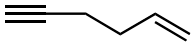
= one pair of H_2

= **1**

- Examples



IHD = 2



IHD = 3

IHD = 2

IHD = 4

16A. Compounds Containing Halogen, Oxygen, or Nitrogen

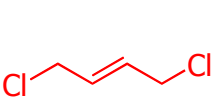
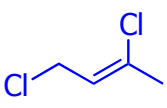
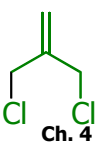
- For compounds containing
  - Halogen – count halogen atoms as though they were hydrogen atoms
  - Oxygen – ignore oxygen atoms and calculate IHD from the remainder of the formula
  - Nitrogen – subtract one hydrogen for each nitrogen atom and ignore nitrogen atoms

- Example 1: IHD of $C_4H_6Cl_2$
  - Count Cl as H
    - $C_4H_6Cl_2 \Rightarrow C_4H_8$
  - A C_4 acyclic alkane: $C_4H_{2(4)+2} = C_4H_{10}$

$\frac{C_4H_{10} - C_4H_8}{H_2}$

IHD of $C_4H_6Cl_2$ = one pair of H_2 = **1**

- Possible structures

 or  or 

... etc.

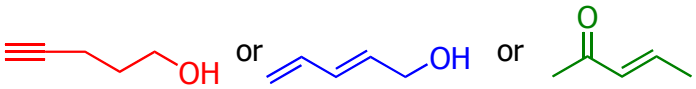
❖ Example 2: IHD of C_5H_8O

- Ignore oxygen
  - ♦ $C_5H_8O \Rightarrow C_5H_8$
- A C_5 acyclic alkane: $C_5H_{2(5)+2} = C_5H_{12}$

$$\begin{array}{r} C_5H_{12} \\ -\ C_5H_8 \\ \hline H_4 \end{array}$$

IHD of $C_4H_6Cl_2$ = two pair of H_2 = **2**

- Possible structures



... etc.

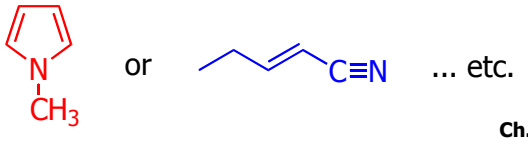
❖ Example 3: IHD of C_5H_7N

- Subtract 1 H for each N
  - ♦ $C_5H_7N \Rightarrow C_5H_6$
- A C_5 acyclic alkane: $C_5H_{2(5)+2} = C_5H_{12}$

$$\begin{array}{r} C_5H_{12} \\ -\ C_5H_6 \\ \hline H_6 \end{array}$$

IHD of $C_4H_6Cl_2$ = three pair of H_2 = **3**

- Possible structures



... etc.

END OF CHAPTER 4