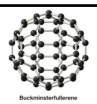
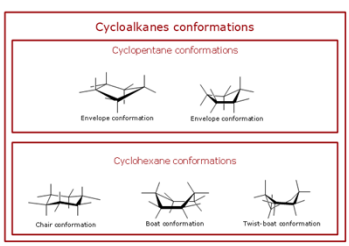
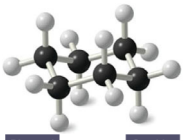
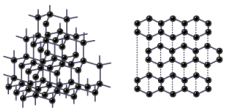
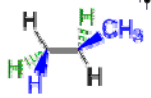
Chapter 3 Alkanes & Cycloalkanes

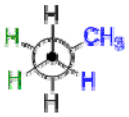




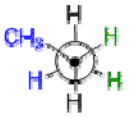








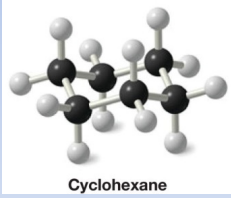
remember hashes are in to the page (back) and wedges are out of the page (forward)



when viewed from the left (methyl group on back C and to the right)

when viewed from the right (methyl group on the front C and to the left)

Table of Contents, Alkanes & Cycloalkanes



Cyclohexane

Sources of Alkanes

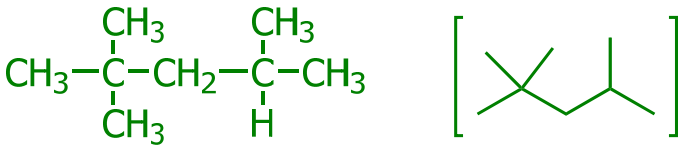
❖ Gasoline

- 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) $\xrightarrow[\sim 500^{o}C]{\text{catalysts}}$ highly branched hydrocarbons (C_5 - C_{10})

❖ Figure 3.13 Fractional distillation of petroleum.

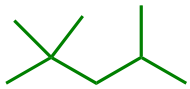
❖ Gasoline (Cont'd)



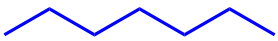
2,2,4-Trimethylpentane (isooctane)
(C_8H_{18})

- 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

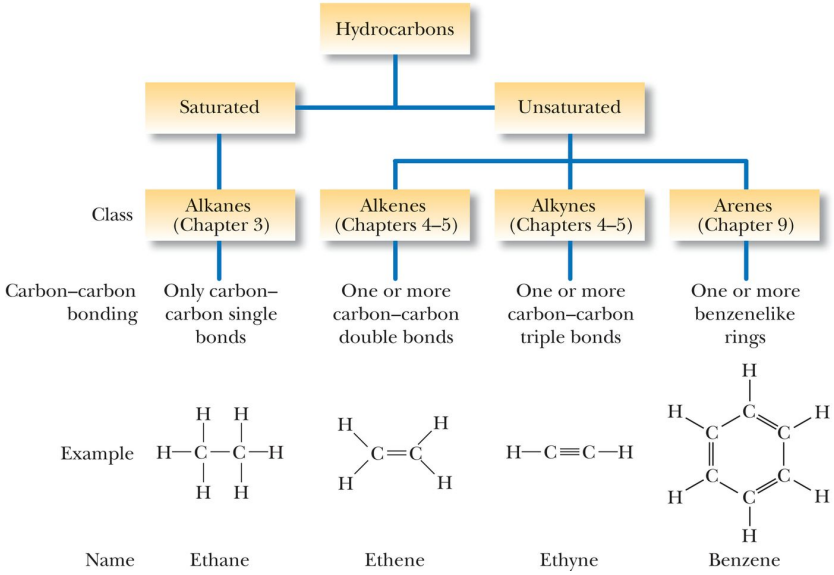
"octane rating"	100	0

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

Structures of Hydrocarbons

- **Hydrocarbon**: A compound composed only of carbon and hydrogen.
- **Saturated hydrocarbon**: A hydrocarbon containing only carbon-carbon single bonds.
- **Alkane**: A saturated hydrocarbon whose carbons are arranged in an open chain.
- **Aliphatic hydrocarbon**: An alternative name for an alkane.

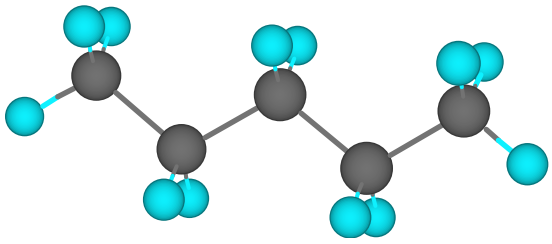
Organic Chemistry



- Figure 3.1 The Four Classes of Hydrocarbons

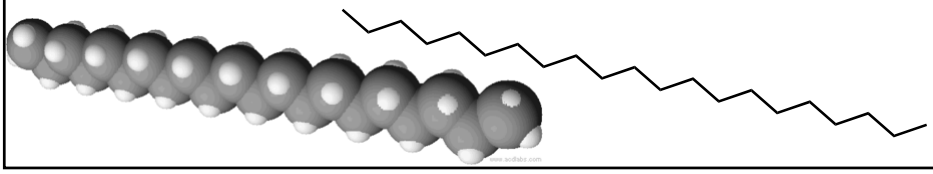
Structure of Alkanes

- Shape
  - Tetrahedral geometry (all carbons are sp^3 hybridized).
  - All bond angles are approximately 109.5°.



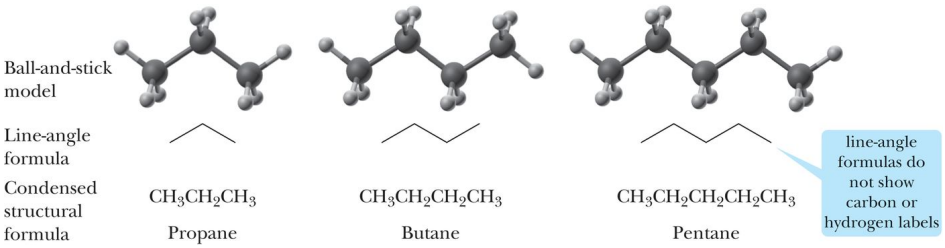
Shapes of Alkanes

- 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, Ex.paraffin ($C_{21}H_{44}$)



Representing Alkanes

- **Line-angle formula**: an abbreviated way to draw structural formulas.
  - Each line represents a single bond.
  - Each line ending represents a CH_3 group.
  - Each vertex (angle) represents a carbon atom.



Alkanes

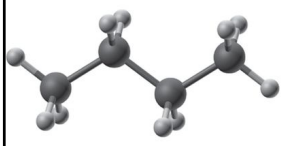
- Alkanes have the general formula C_nH_{2n+2}

TABLE 3.1 Names, Molecular Formulas, and Condensed Structural Formulas for the First 20 Alkanes with Unbranched Chains

Name	Molecular Formula	Condensed Structural Formula	Name	Molecular Formula	Condensed Structural Formula
methane	CH_4	CH_4	undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$
ethane	C_2H_6	CH_3CH_3	dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
propane	C_3H_8	$CH_3CH_2CH_3$	tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

Constitutional Isomers

- **Constitutional isomers**: Compounds with the same molecular formula but a different connectivity of their atoms.
  - There are two constitutional isomers with the molecular formula C_4H_{10}.

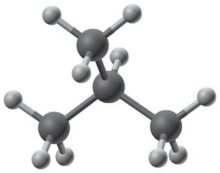


$CH_3CH_2CH_2CH_3$

Butane
(boiling point
= –0.5 °C)

CH_3
|
CH_3CHCH_3

2-Methylpropane
(boiling point
= –11.6 °C)



Constitutional Isomerism

- The potential for constitutional isomerism from just the elements carbon and hydrogen is enormous.

Carbon Atoms	Constitutional Isomers
1	0
5	3
10	75
15	4,347
25	36,797,588

IUPAC Nomenclature

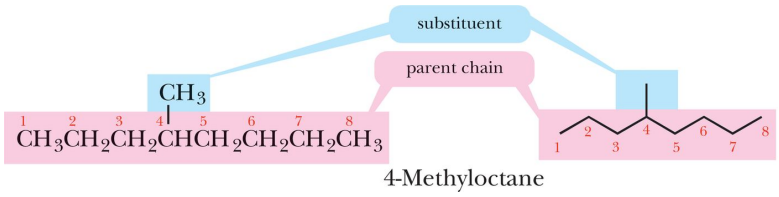
- **Suffix *-ane*** specifies an alk**ane**.
- **Prefix** tells the number of carbon

TABLE 3.2 Prefixes Used in the IUPAC System to Show the Presence of 1 to 20 Carbons in an Unbranched Chain

Prefix	Number of Carbon Atoms	Prefix	Number of Carbon Atoms
meth-	1	undec-	11
eth-	2	dodec-	12
prop-	3	tridec-	13
but-	4	tetradec-	14
pent-	5	pentadec-	15
hex-	6	hexadec-	16
hept-	7	heptadec-	17
oct-	8	octadec-	18
non-	9	nonadec-	19
dec-	10	eicos-	20

IUPAC Nomenclature

- **Parent name** The longest carbon chain.
- **Substituent**: A group bonded to the parent chain.
  - **Alkyl group**: A substituent derived by removal of a hydrogen from an alkane; given the symbol **R-**.
  - CH_4 becomes CH_3- (methyl).
  - CH_3CH_3 becomes CH_3CH_2- (ethyl).



4-Methyloctane

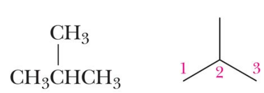
IUPAC Nomenclature

TABLE 3.3 Names of the Most Common Alkyl Groups

Name	Condensed Structural Formula	Name	Condensed Structural Formula
methyl	$-CH_3$	isobutyl	$-CH_2CHCH_3$ | CH_3
ethyl	$-CH_2CH_3$	*sec*-butyl (abbreviation for "secondary")	$-CHCH_2CH_3$ | CH_3
propyl	$-CH_2CH_2CH_3$	*tert*-butyl (abbreviation for "tertiary")	CH_3 | $-CCH_3$ | CH_3
isopropyl	$-CHCH_3$ | CH_3		
butyl	$-CH_2CH_2CH_2CH_3$		

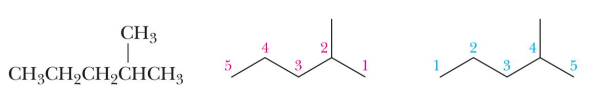
IUPAC Nomenclature

1. The name of an alkane with an unbranched chain consists of a prefix and the suffix -*ane*.
2. For branched alkanes, the parent chain is the longest chain of carbon atoms.
3. Each substituent is given a name and a number.



2-Methylpropane

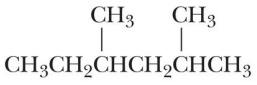
4. If there is one substituent, number the chain from the end that gives it the lower number.

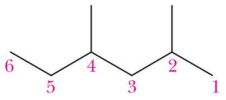


2-Methylpentane (not 4-methylpentane)

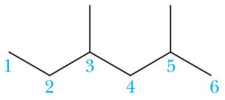
IUPAC Nomenclature

5. If there are two or more identical substituents, number the parent chain from the end that gives the lower number to the substituent encountered first. The number of times the substituent occurs is indicated by the prefixes *di-*, *tri-*, *tetra-*, and so on.





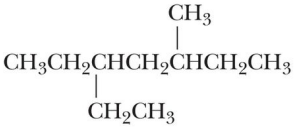
2,4-Dimethylhexane

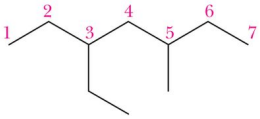


(not 3,5-dimethylhexane)

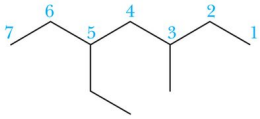
IUPAC Nomenclature

6. If there are two or more different substituents,
- list them in alphabetical order.
- number from the end of the chain that gives the substituent encountered first the lower number.





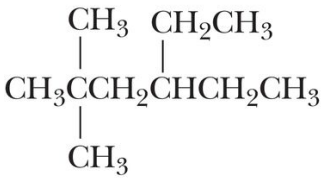
3-Ethyl-5-methylheptane

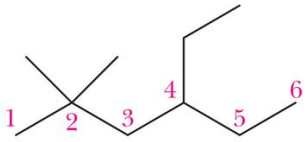


(not 3-methyl-5-ethylheptane)

IUPAC Nomenclature

7. The prefixes *di-*, *tri-*, *tetra-*, etc. are not included in alphabetization. Iso, as in isopropyl, is included in alphabetization. In the following example, the alphabetizing names are ethyl and methyl.

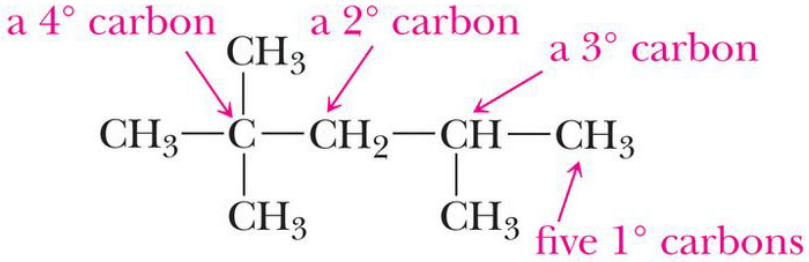




4-Ethyl-2,2-dimethylhexane
(not 2,2-dimethyl-4-ethylhexane)

Classification of Carbons

- **Primary (1°)**: a C bonded to one other carbon.
- **Secondary (2°)**: a C bonded to two other carbons.
- **Tertiary (3°)**: a C bonded to three other carbons.
- **Quaternary (4°)**: a C bonded to four other carbons.



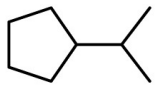
2,2,4-Trimethylpentane

Cycloalkanes

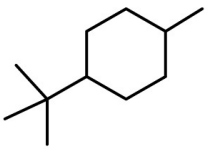
- General formula C_nH_{2n}
  - Five- and six-membered rings are the most common.
- Structure and nomenclature
  - Prefix the name of the corresponding open-chain alkane with **cyclo**-, name each substituent on the ring.
  - If only one substituent, no need to give it a number.
  - If two substituents, number the ring from the substituent of lower alphabetical order.
  - If three or more substituents, number the ring to give them the lowest set of numbers, and then list them in alphabetical order.

Cycloalkanes

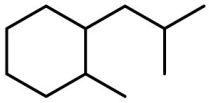
- Commonly written as line-angle formulas
  - examples:



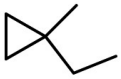
Isopropylcyclopentane



1-*tert*-Butyl-4-methyl-cyclohexane



1-Isobutyl-2-methyl-cyclohexane



1-Ethyl-1-methyl-cyclopropane

IUPAC- A General System

- prefix-infix-suffix
  - **Prefix** tells the number of carbon atoms in the parent.
  - **Infix** tells the nature of the carbon-carbon bonds.
  - **Suffix** tells the class of compound.

Infix	Nature of Carbon–Carbon Bonds in the Parent Chain
-an-	all single bonds
-en-	one or more double bonds
-yn-	one or more triple bonds

keep in mind that the infix refers to the nature of the *C–C bonds in the parent chain*

IUPAC- A General System

- prefix-infix-suffix
  - **Prefix** tells the number of carbon atoms in the parent.
  - **Infix** tells the nature of the carbon-carbon bonds.
  - **Suffix** tells the class of compound.

Suffix	Class of Compound
-e	hydrocarbon
-ol	alcohol
-al	aldehyde
-one	ketone
-oic acid	carboxylic acid

we will learn suffixes for other classes of compounds in later chapters

IUPAC - a general system

$CH_3CH{=}CH_2$

prop-**en**-**e** = propene

eth-**an**-**ol** = ethanol CH_3CH_2OH

but-**an**-**one** = butanone

but-**an**-**al** = butanal

but-**an**-**oic acid** = butanoic acid

cyclohex-**an**-**ol** = cyclohexanol

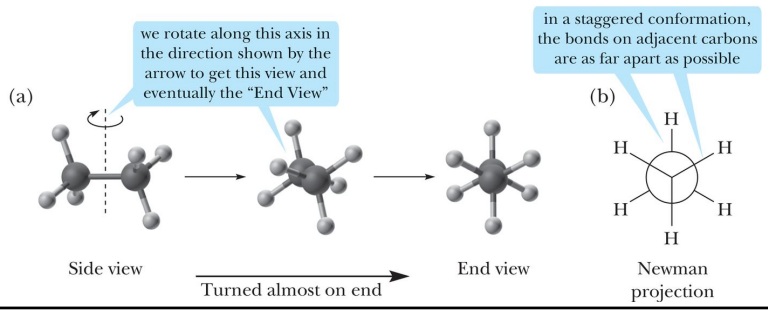
eth-**yn**-**e** = ethyne $CH{\equiv}CH$

eth-**an**-**amine** = ethanamine

$CH_3CH_2NH_2$

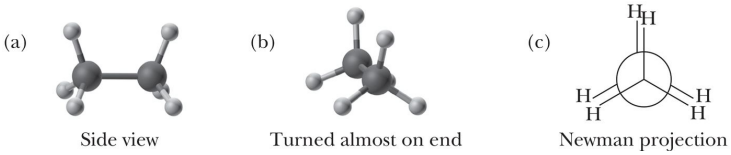
Conformation

- **Conformation**: Any three-dimensional arrangement of atoms in a molecule that results from rotation about a single bond.
  - **Staggered conformation**: A conformation about a carbon-carbon single bond where the atoms on one carbon are as far apart as possible from the atoms on an adjacent carbon. On the right is a **Newman projection** formula.

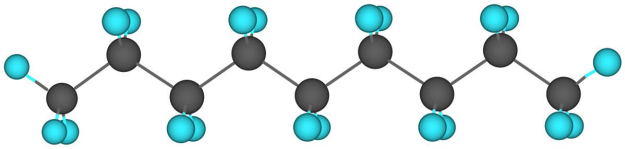


Conformation

- **Eclipsed conformation**: A conformation about a carbon-carbon single bond in which the atoms on one carbon are as close as possible to the atoms on an adjacent carbon.

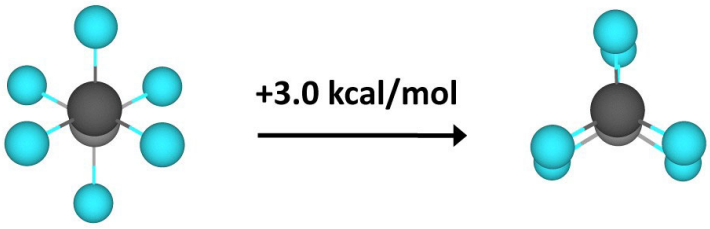


- The lowest energy conformation of an alkane is a fully **Staggered conformation**.



Conformations

- **Torsional strain**: Strain that arises when nonbonded atoms separated by three bonds are forced from a staggered conformation to an eclipsed conformation.
  - Also called **eclipsed interaction strain**.
  - The torsional strain between staggered and eclipsed ethane is approximately 12.6 kJ/mol(3.0 kcal/mol).



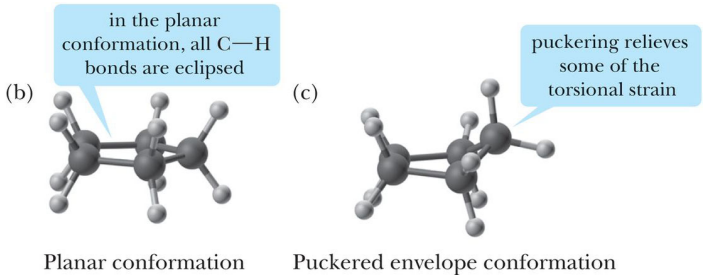
Cycloalkanes

- Cyclopentane
  - In planar cyclopentane, all C-C-C bond angles are 108°, which differ only slightly from the tetrahedral angle of 109.5°.
  - Consequently there is little angle strain.
  - **Angle strain**: Strain that arises when a bond angle is either compressed or expanded compared with its optimal value.

(a)

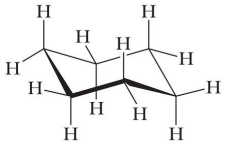
Cycloalkanes

- Cyclopentane (cont'd)
  - In planar cyclopentane, there are 10 fully eclipsed C-H bonds creating a torsional strain of approximately 42 kJ/mol (10 kcal/mol).
  - Puckering to an "envelope" conformation relieves part of this strain
  - In an envelope conformation, eclipsed interactions are reduced but angle strain is increased slightly (105°).

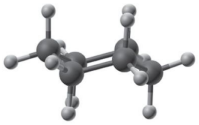


Cycloalkanes

- Cyclohexane
  - The most stable conformation is a puckered conformation called a **chair conformation**.
  - In a chair conformation, all bond angles are approx. 109.5° and all bonds on adjacent carbons are staggered.



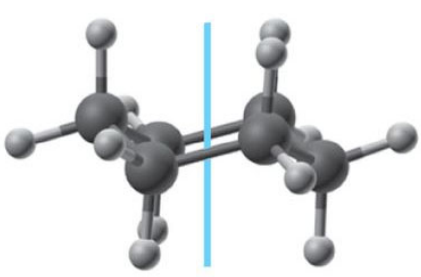
Skeletal model

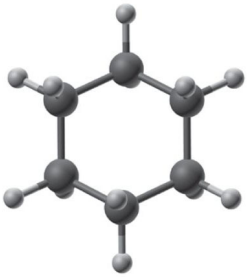


Ball-and-stick model viewed from the side

Cycloalkanes

- Chair cyclohexane
  - Six C–H bonds are equatorial and six are axial.

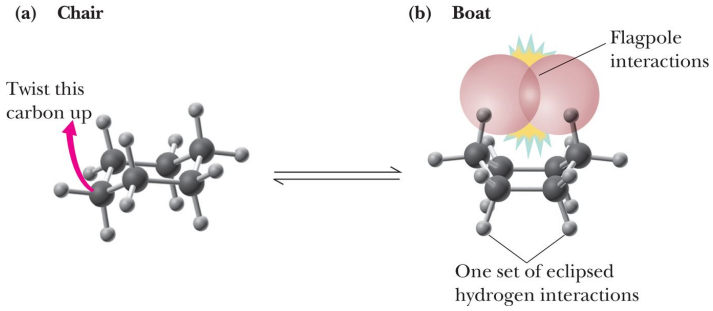




  - An equatorial bond extends from the ring roughly perpendicular to the imaginary axis of the ring.
  - An axial bond extends from the ring roughly parallel to the imaginary axis of the ring.

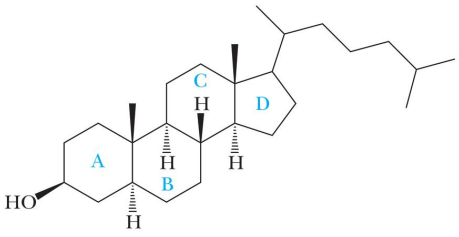
Cyclohexane

- **Boat conformation**: A puckered conformation in which carbons 1 & 4 are bent toward each other.
  - A boat conformation is less stable than a chair conformation by 27 kJ/mol (6.5 kcal/mol).
  - **Torsional strain** is created by four sets of eclipsed hydrogen interactions.
  - **Steric strain** (nonbonded interaction strain) is created by one set of flagpole interactions.

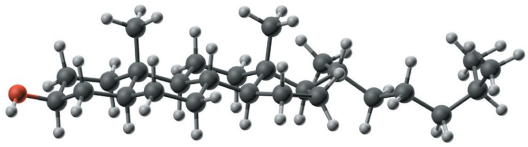


Cyclohexane

- Following is a structural formula and ball-and-stick model of cholestanol, a close relative of cholesterol. Describe the conformation of each ring in cholestanol.

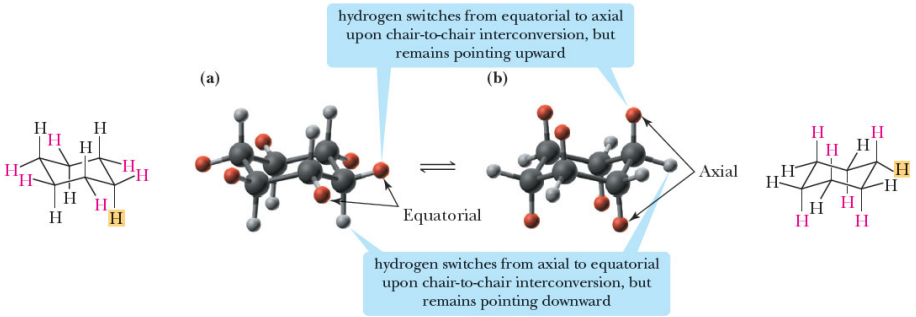


Cholestanol



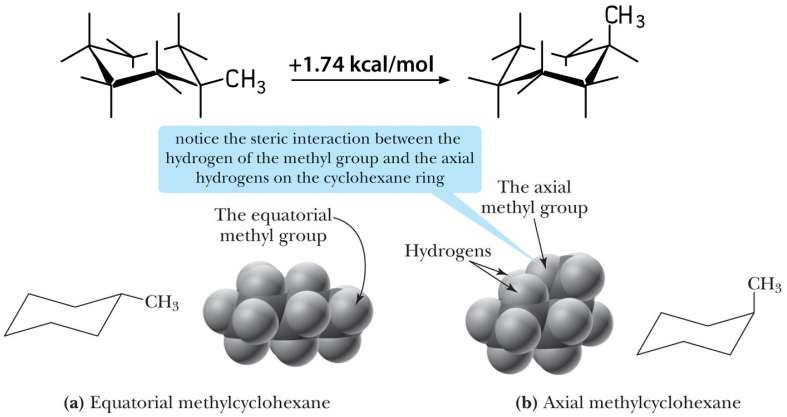
Cyclohexane

- chair cyclohexane (cont'd)
  - There are two equivalent chair conformations.
  - The alternative chair conformation interconvert via a boat conformation.
  - All C–H bonds that are equatorial in one chair are axial in the alternative chair, and vice versa.



Methylcyclohexane

- A group equatorial in one chair is axial in the alternative chair.
- The two chairs are no longer of equal stability. They differ by 7.28 kJ/mol (1.74 kcal/mol)

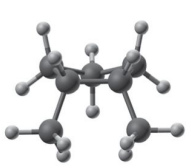


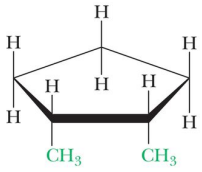
Cis-trans Isomerism

- *Cis-trans* isomers have
  - The same molecular formula.
  - The same connectivity of their atoms.
  - An arrangement of atoms in space that cannot be interconverted by rotation about sigma bonds.

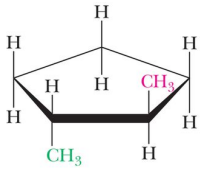
Cis-trans isomerism

- A cyclopentane ring is commonly viewed through an edge or from above.

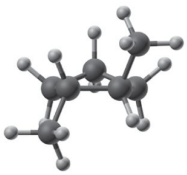


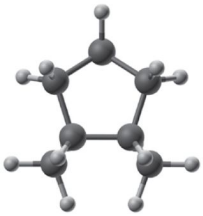


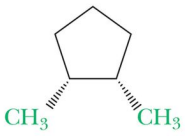
cis-1,2-Dimethyl-cyclopentane



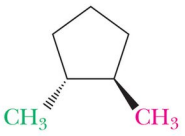
trans-1,2-Dimethyl-cyclopentane



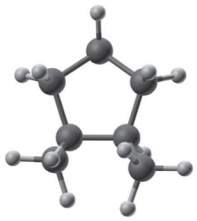




cis-1,2-Dimethyl-cyclopentane



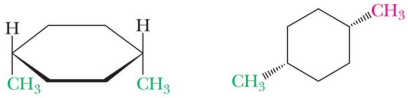
trans-1,2-Dimethyl-cyclopentane



Cis-trans isomerism

- A cyclohexane ring is commonly viewed as a planar hexagon viewed from the side or from above.

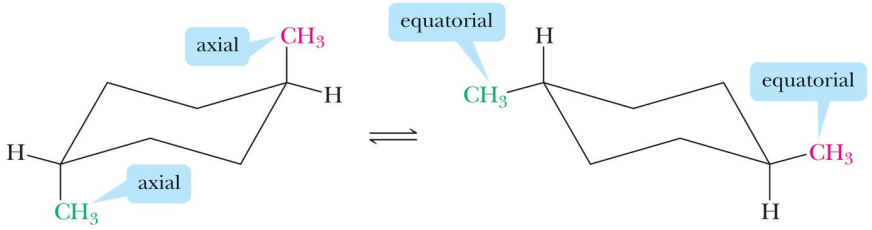
trans-1,4-Dimethylcyclohexane



cis-1,4-Dimethylcyclohexane

Cis-trans isomerism

- Or we can represent a cyclohexane as a chair conformation.
- In viewing chair conformations, groups equatorial in one chair are axial in the alternative chair.
- For *trans*-1,4-dimethylcyclohexane, the diequatorial chair is more stable than the diaxial chair.

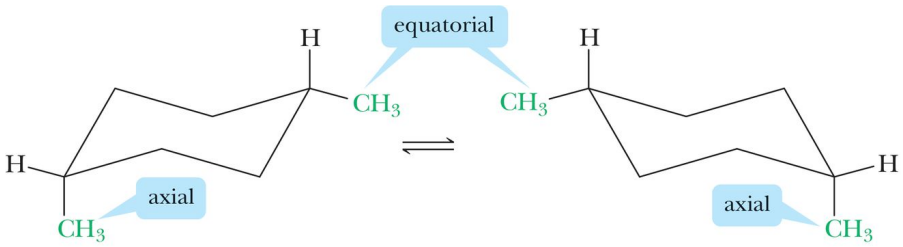


(less stable) (more stable)

trans-1,4-Dimethylcyclohexane

Cis-trans isomerism

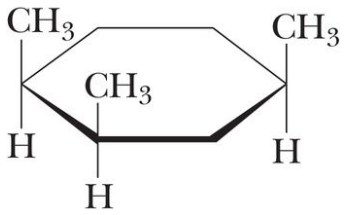
- For *cis*-1,4-dimethylcyclohexane, the alternative chairs are of equal stability.



cis-1,4-Dimethylcyclohexane
(these conformations are of equal stability)

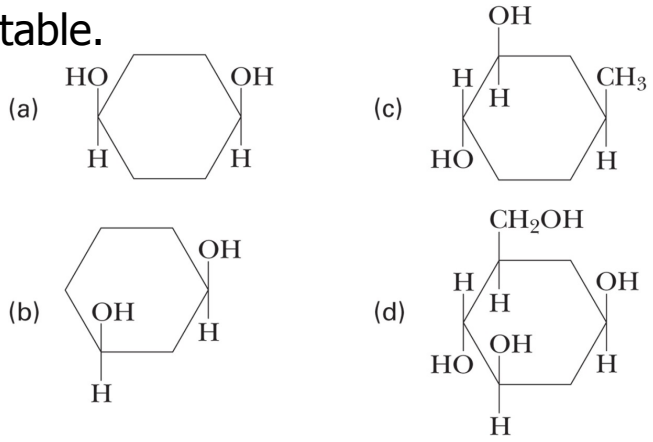
Cis-trans isomerism

- **Problem 3.11**: Draw the alternative chair conformations of this trisubstituted cyclohexane, and state which conformation is the more stable.



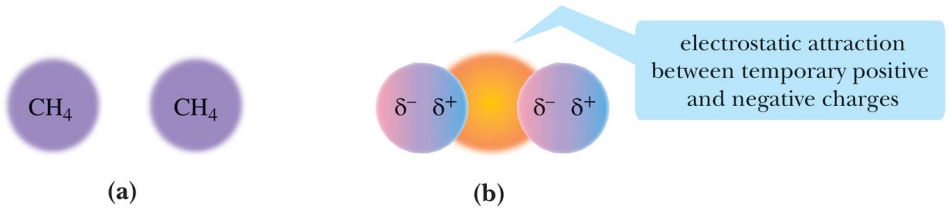
Conformation of Cyclohexanes

- **Problem**: Draw alternative chair conformations of each substituted cyclo-alkane, and state which conformation of each is the more stable.



Physical Properties

- Alkanes are nonpolar compounds and have only weak interactions between their molecules.
- **Dispersion forces**: Weak intermolecular forces of attraction resulting from interaction of temporary induced dipoles.



Physical Properties

- Boiling point
  - Low-molecular-weight alkanes (1 to 4 carbons) are gases at room temperature; e.g., methane, propane, butane.
  - Higher-molecular-weight alkanes (5 to 17 carbons) are liquids at room temperature (e.g., hexane, decane, gasoline, kerosene).
  - High-molecular-weight alkanes (18 or more carbons) are white, waxy semisolids or solids at room temperature (e.g., paraffin wax).
- Density
  - Average density is about 0.7 g/mL.
  - Liquid and solid alkanes float on water.

Physical Properties

- Constitutional isomers are different compounds and have different physical properties.

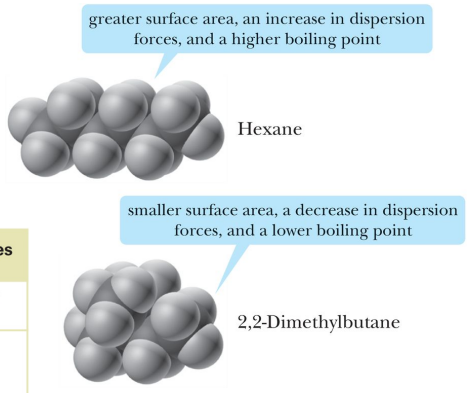


TABLE 3.5 Physical Properties of the Isomeric Alkanes with the Molecular Formula C_6H_{14}

Name	Melting Point (°C)	Boiling Point (°C)	Density (g/mL)
hexane	−95	69	0.659
3-methylpentane	−118	64	0.664
2-methylpentane	−154	62	0.653
2,3-dimethylbutane	−129	58	0.662
2,2-dimethylbutane	−100	50	0.649

Reactions of Alkanes

- Oxidation is the basis for the use of alkanes as energy sources for heat and power.
  - **Heat of combustion**: the heat released when one mole of a substance is oxidized to carbon dioxide and water.

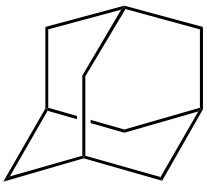
when balancing equations for combustion reactions of hydrocarbons, first balance the number of carbons, next balance the number of hydrogens, then balance the number of oxygens. If the equation is still not balanced, consider doubling all coefficients on each side of the equation arrow

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \Delta H^\circ = -886\ kJ/mol (-212\ kcal/mol)$

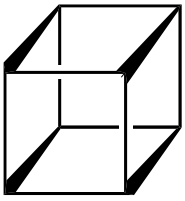
Methane

$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O \quad \Delta H^\circ = -2{,}220\ kJ/mol (-530\ kcal/mol)$

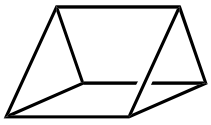
Propane



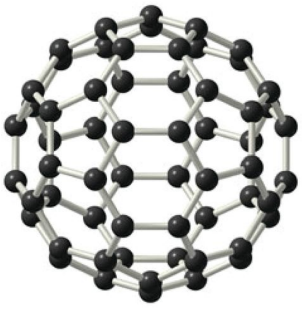
Adamantane



Cubane



Prismane



C_{60} (Buckminsterfullerene)