WILLIAM H. BROWN
THOMAS POON

www.wiley.com/college/brown

CHAPTER THREE

Alkanes and Cycloalkanes

1

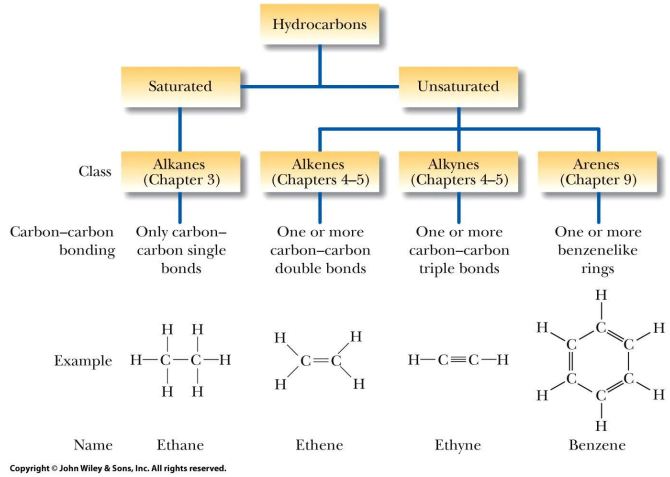
Structure

- **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.

2

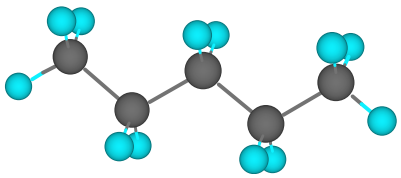
Organic Chemistry

- Figure 5.1 The Four Classes of Hydrocarbons



Structure of Alkanes

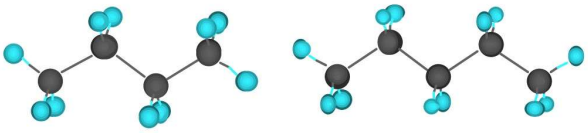
- Shape
  - Tetrahedral geometry (all carbons are sp^3 hybridized).
  - All bond angles are approximately 109.5°.



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.

Ball-and-stick model



Line-angle formula

Structural formula

$CH_3CH_2CH_2CH_3$ **Butane**

$CH_3CH_2CH_2CH_2CH_3$ **Pentane**

WILEY

3-5

5

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	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

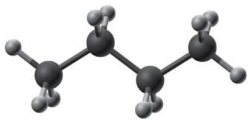
WILEY

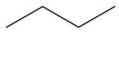
3-6

6

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}.



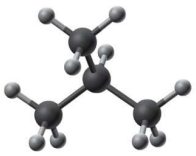


$CH_3CH_2CH_2CH_3$

Butane
(boiling point
= –0.5 °C)

CH_3
|
CH_3CHCH_3

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



WILEY

3-7

7

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

WILEY

3-8

8

EXAMPLE 3.1

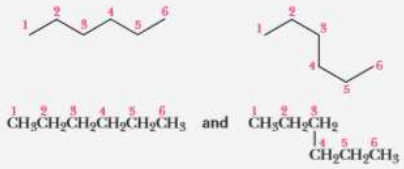
Do the structural formulas in each pair represent the same compound or constitutional isomers?

(a) $CH_3CH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2CH_2CH(CH_2CH_2CH_3)$ (each is C_6H_{14})

(b) $CH_3CHCH_2CH(CH_3)CH_3$ and $CH_3CH_2CH(CH_3)CHCH_3$ (each is C_7H_{16})

SOLUTION

(a) Each structural formula has an unbranched chain of six carbons. The two structures are identical and represent the same compound:



(b) Each structural formula has a chain of five carbons with two CH_3 branches. Although the branches are identical, they are at different locations on the chains. Therefore, these structural formulas represent constitutional isomers:

9

IUPAC Nomenclature

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

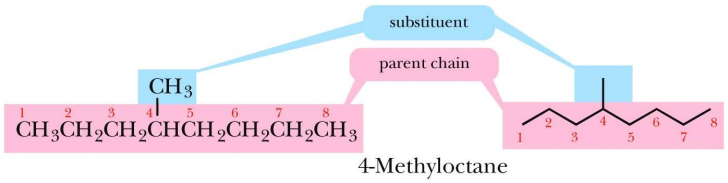
TABLE 3.2 Prefixes Used in the IUPAC System to Show the Presence of 1 to 20 Carbons in an Unbranched Chain

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

10

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

WILEY 3-11

11

IUPAC Nomenclature

TABLE 3.3 Names of the Most Common Alkyl Groups

Name	Condensed Structural Formula	Name	Condensed Structural Formula
methyl	$-CH_3$	isobutyl	$-CH_2CH(CH_3)_2$
ethyl	$-CH_2CH_3$	*sec*-butyl	$-CH(CH_3)CH_2CH_3$
propyl	$-CH_2CH_2CH_3$	*tert*-butyl	$-C(CH_3)_3$
isopropyl	$-CH(CH_3)_2$		
butyl	$-CH_2CH_2CH_2CH_3$		

abbreviation for "secondary"

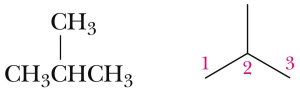
abbreviation for "tertiary"

WILEY 3-12

12

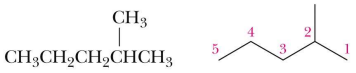
IUPAC Nomenclature

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.



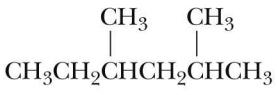
2-Methylpentane

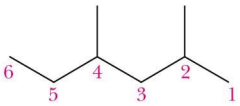
WILEY 3-13

13

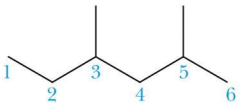
IUPAC Nomenclature

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



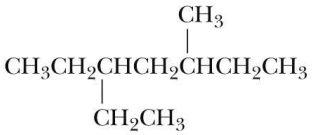
(not 3,5-dimethylhexane)

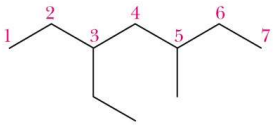
WILEY 3-14

14

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.

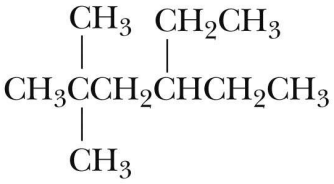


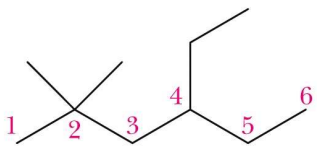


3-Ethyl-5-methylheptane

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.

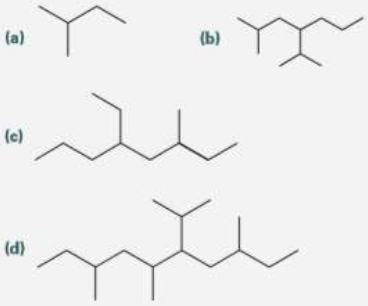




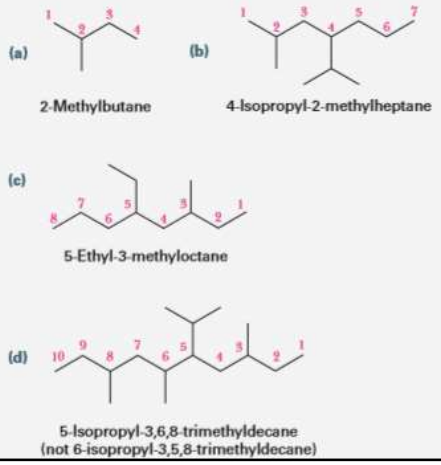
4-Ethyl-2,2-dimethylhexane
(not 2,2-dimethyl-4-ethylhexane)

EXAMPLE 3.3

Write IUPAC names for these alkanes:



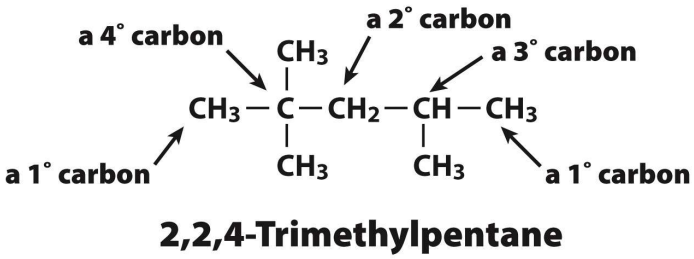
SOLUTION



17

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.



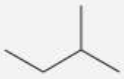
2,2,4-Trimethylpentane

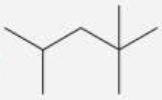
3-18

18

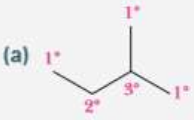
EXAMPLE 3.4

Classify each carbon atom in the following compounds as 1°, 2°, 3°, or 4°.

(a) 

(b) 

SOLUTION

(a) 

(b) 

 3-19

19

Cycloalkanes

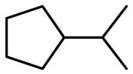
- General formula C_nH_{2n}
  - Five- and six-membered rings are the most common.
- Structure and nomenclature
  - Prefix the name of the corresponding open-chain alkane with **cyclo**-, name each substituent on the ring.
  - If only one substituent, no need to give it a number.
  - If two substituents, 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.

 3-20

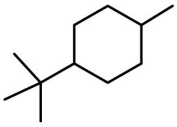
20

Cycloalkanes

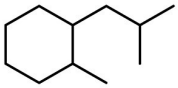
- Commonly written as line-angle formulas
  - examples:



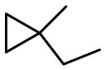
Isopropylcyclopentane



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

WILEY 3-23

23

IUPAC - a general system

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

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

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

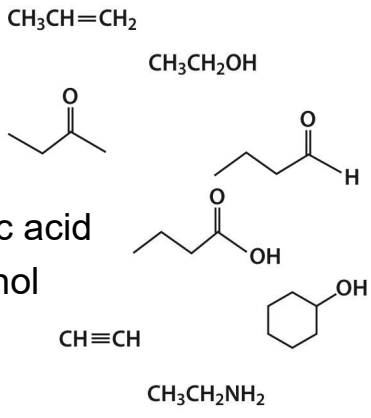
but-**an**-**al** = butanal

pent-**an**-**oic** acid = pentanoic acid

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

eth-**yn**-**e** = ethyne

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

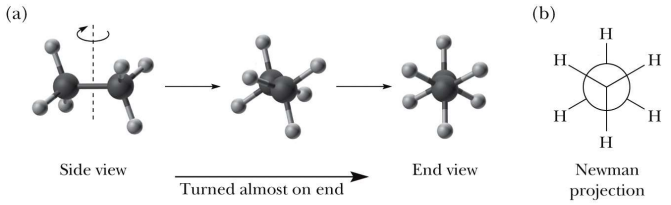


WILEY 3-24

24

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.

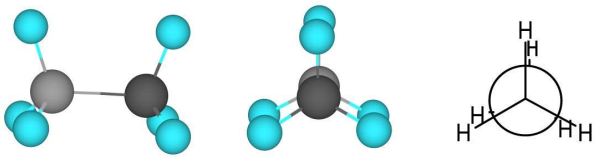


WILEY 3-25

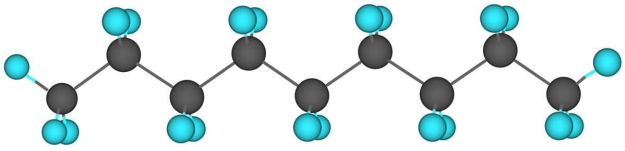
25

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.

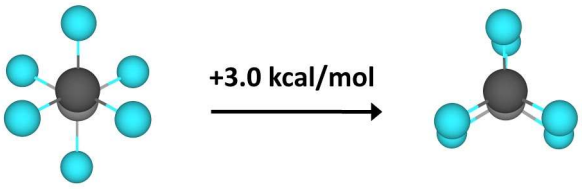


WILEY 3-26

26

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).

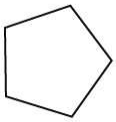


WILEY 3-27

27

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.

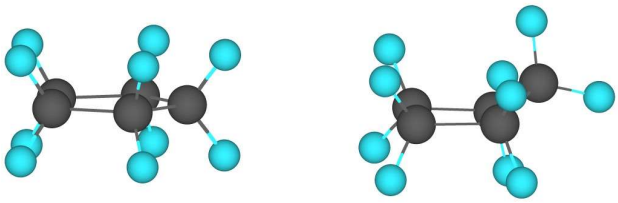


WILEY 3-28

28

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°).



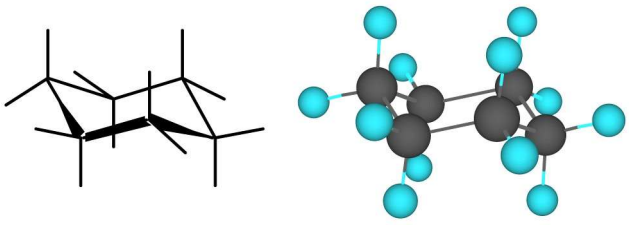
WILEY

3-29

29

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.



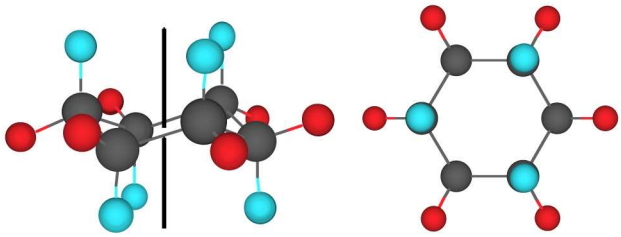
WILEY

3-30

30

Cycloalkanes

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



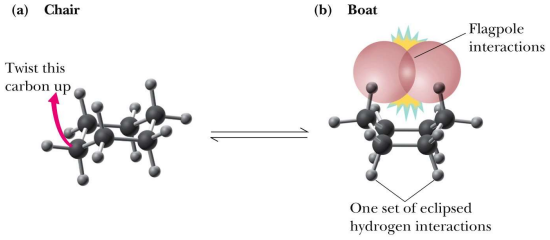
  - An equatorial bond extends from the ring roughly perpendicular to the imaginary axis of the ring.
  - An axial bond extends from the ring roughly parallel to the imaginary axis of the ring.

WILEY 3-31

31

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.

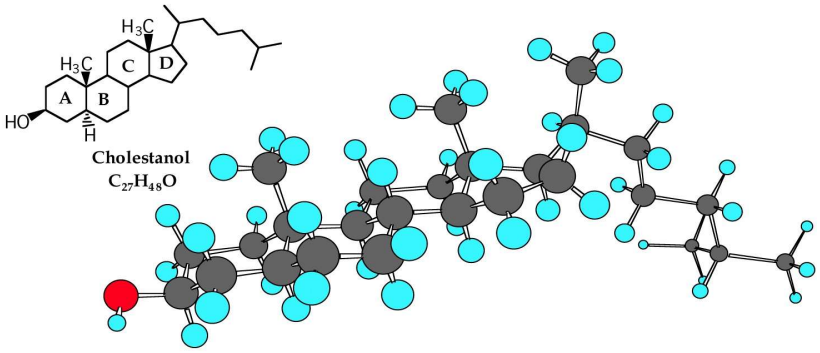


WILEY 3-32

32

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.

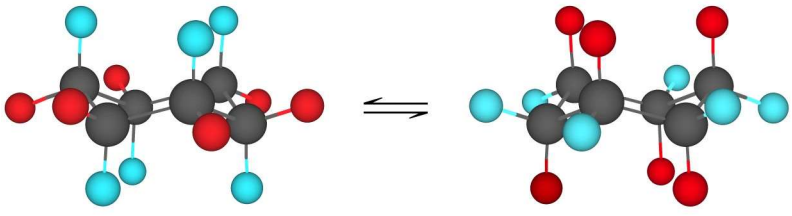


3-33

33

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.



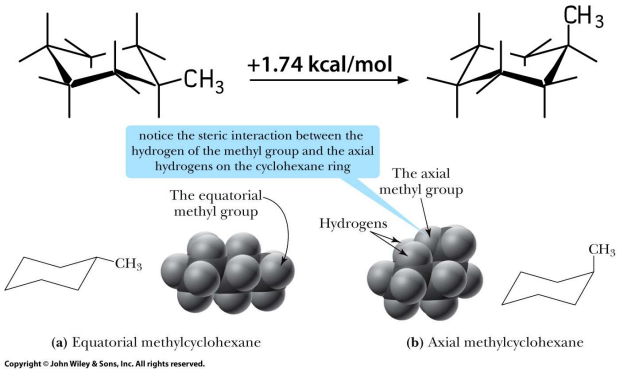
3-34

34

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)



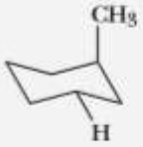
WILEY

3-35

35

EXAMPLE 3.8

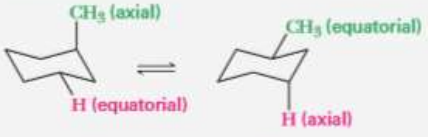
Following is a chair conformation of cyclohexane showing a methyl group and one hydrogen:



(a) Indicate by a label whether each group is equatorial or axial.

(b) Draw the other chair conformation, and again label each group as equatorial or axial.

SOLUTION



WILEY

36

Cis-trans Isomerism

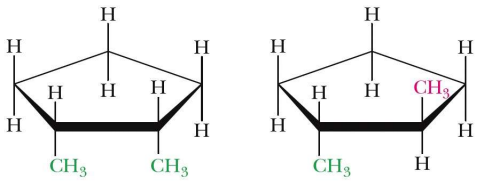
- *Cis-trans* isomers have
  - The same molecular formula.
  - The same connectivity of their atoms.
  - An arrangement of atoms in space that cannot be interconverted by rotation about sigma bonds.

WILEY 3-37

37

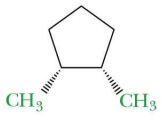
Cis-trans isomerism

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

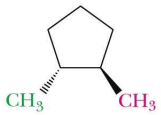


cis-1,2-Dimethyl-cyclopentane

trans-1,2-Dimethyl-cyclopentane



cis-1,2-Dimethyl-cyclopentane



trans-1,2-Dimethyl-cyclopentane

WILEY 3-38

38

Cis-trans isomerism

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

trans-1,4-Dimethylcyclohexane

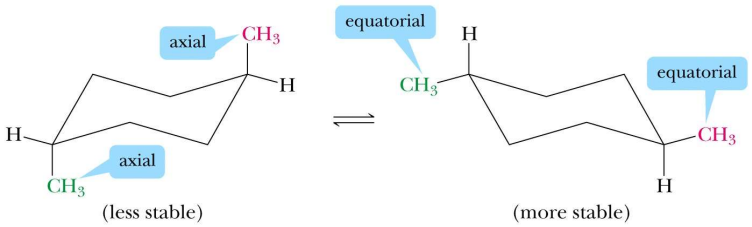
cis-1,4-Dimethylcyclohexane

3-39

39

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.



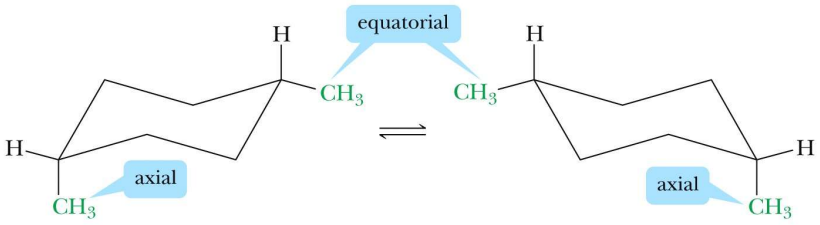
trans-1,4-Dimethylcyclohexane

3-40

40

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)

WILEY 3-41

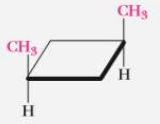
41

EXAMPLE 3.10

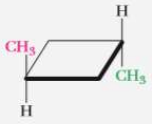
Which cycloalkanes show *cis–trans* isomerism? For each that does, draw both isomers.
(a) Methylcyclopentane (b) 1,1-Dimethylcyclobutane (c) 1,3-Dimethylcyclobutane

SOLUTION

(a) Methylcyclopentane does not show *cis–trans* isomerism: It has only one substituent on the ring.
(b) 1,1-Dimethylcyclobutane does not show *cis–trans* isomerism: Only one arrangement is possible for the two methyl groups on the ring, and they must be *trans*.
(c) 1,3-Dimethylcyclobutane shows *cis–trans* isomerism. Note that, in these structural formulas, we show only the hydrogens on carbons bearing the methyl groups.



cis-1,3-Dimethylcyclobutane



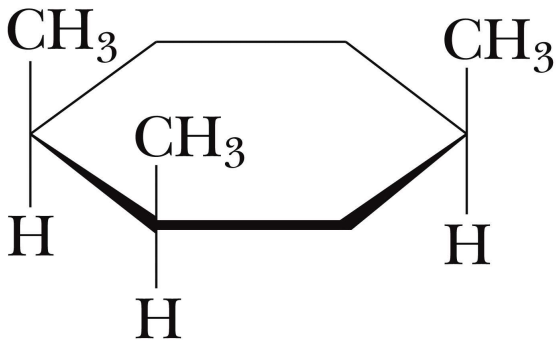
trans-1,3-Dimethylcyclobutane

WILEY 3-42

42

Cis-trans isomerism

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

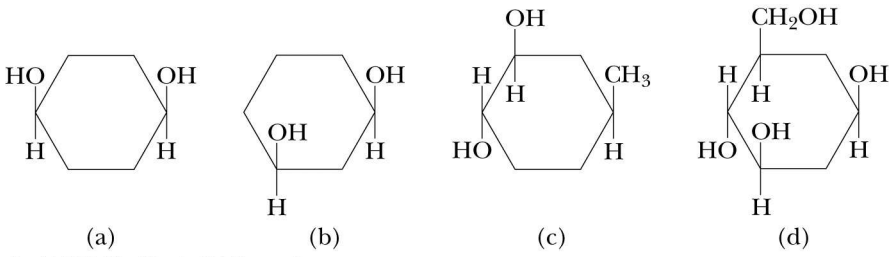


WILEY 3-43

43

Conformation of Cyclohexanes

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

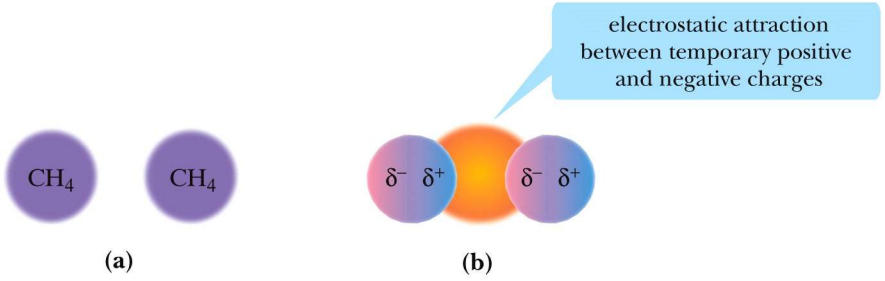


WILEY 3-44

44

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.



WILEY 3-45

45

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.

WILEY 3-46

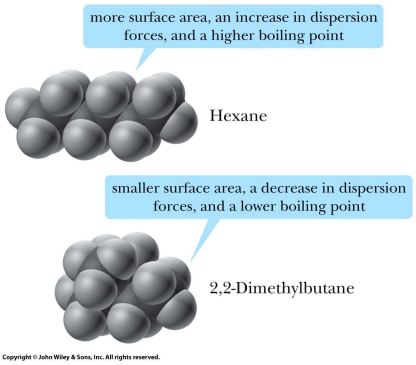
46

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.

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

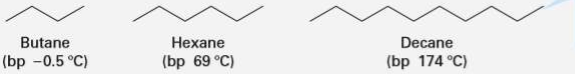
$$\underset{\text{Propane}}{CH_3CH_2CH_3} + 5O_2 \longrightarrow 3CO_2 + 4H_2O \quad \Delta H^\circ = -2{,}220\ \text{kJ/mol}(-530\ \text{kcal/mol})$$

EXAMPLE 3.12

Arrange the alkanes in each set in order of increasing boiling point:
(a) Butane, decane, and hexane (b) 2-Methylheptane, octane, and 2,2,4-trimethylpentane

SOLUTION

(a) All of the compounds are unbranched alkanes. As the number of carbon atoms in the chain increases, the dispersion forces among molecules increase, and the boiling points increase. Decane has the highest boiling point, butane the lowest:



Butane (bp −0.5 °C) Hexane (bp 69 °C) Decane (bp 174 °C)

in unbranched hydrocarbons, the longer the chain length, the higher is the surface area. This results in an increase in the dispersion forces and an increase in boiling point

(b) These three alkanes are constitutional isomers with the molecular formula C_8H_{18}. Their relative boiling points depend on the degree of branching. 2,2,4-Trimethylpentane, the most highly branched isomer, has the smallest surface area and the lowest boiling point. Octane, the unbranched isomer, has the largest surface area and the highest boiling point.

WILEY 3-49

49

Sources of Alkanes

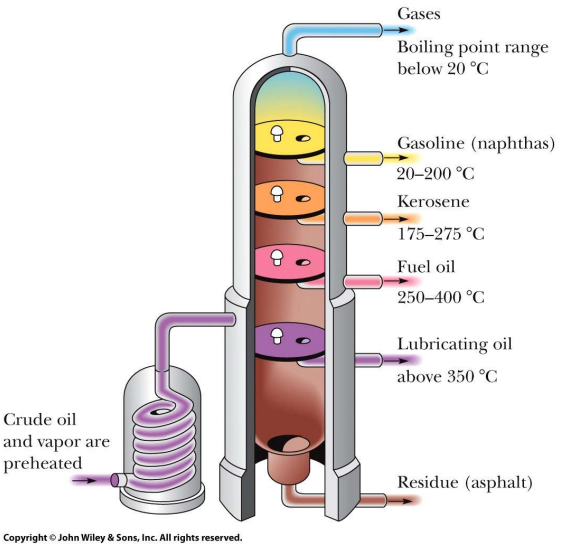
- Natural gas
  - 90–95% methane, 5-10% ethane
- Petroleum
  - Gases (bp below 20 °C)
  - Naphthas, including gasoline (bp 20–200 °C)
  - Kerosene (bp 175–275 °C)
  - Fuel oil (bp 250–400 °C)
  - Lubricating oils (bp above 350 °C)
  - Asphalt (residue after distillation)
- Coal

WILEY 3-50

50

Sources of Alkanes

- Figure 3.13 Fractional distillation of petroleum.



WILEY

3-51

51

Synthesis Gas

– **Synthesis gas**: A mixture of carbon monoxide and hydrogen in varying proportions, depending on how it is produced.

$$\underset{\text{Coal}}{C} + H_2O \xrightarrow{\text{heat}} CO + H_2$$

$$\underset{\text{Methane}}{CH_4} + \frac{1}{2}O_2 \xrightarrow{\text{catalyst}} CO + 2H_2$$

– Methanol and acetic acid are produced from synthesis gas.

$$CO + 2H_2 \xrightarrow{\text{catalyst}} \underset{\text{Methanol}}{CH_3OH}$$

$$\underset{\text{Methanol}}{CH_3OH} + CO \xrightarrow{\text{catalyst}} \underset{\text{Acetic acid}}{CH_3\overset{\overset{O}{\|}}{C}OH}$$

WILEY

3-52

52

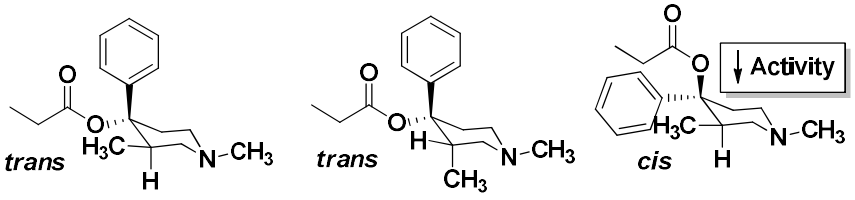
Methane Economy

- If the United States moves from a petroleum economy to a natural gas economy as some advocate, synthesis gas and synthesis gas-derived methanol will become key building blocks.

 3-53

53

MC example of Meperidine chair conformations



 3-54

54