

Organic Chemistry, *Fourth Edition*

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Chapter 4 Alkanes (Acyclic Alkanes and Cycloalkanes)

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The University of Illinois - Springfield

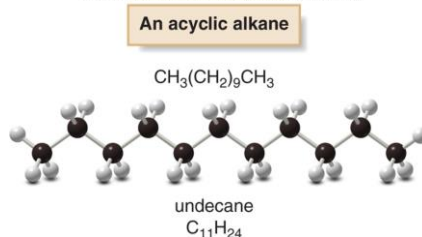
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1

Acyclic Alkanes

- Alkanes are aliphatic hydrocarbons having only C-C and C-H σ bonds. They can be categorized as acyclic or cyclic.
- Acyclic alkanes have the molecular formula C_nH_{2n+2} (where n = an integer).
 - They contain only linear and branched chains of carbon atoms.
 - They are also called saturated hydrocarbons because they have the maximum number of hydrogen atoms per carbon.

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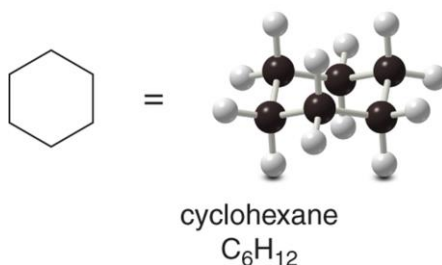
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Cycloalkanes

- **Cycloalkanes** contain carbons joined in one or more rings.
- Because their general formula is C_nH_{2n} , they have two fewer H atoms than an acyclic alkane with the same number of carbons.

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A cycloalkane

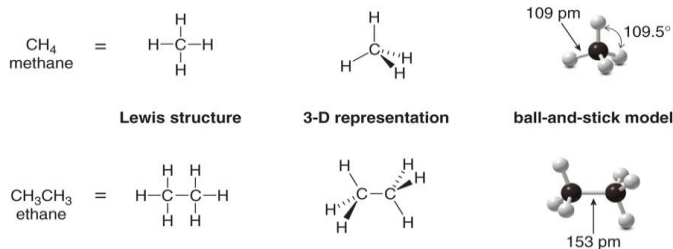


3

Tetrahedral Geometry of Carbon

- All C atoms in an alkane are surrounded by four groups, making them sp^3 hybridized and tetrahedral, with all bond angles of 109.5° .
- The 3-D representations and ball-and-stick models for these alkanes indicate the tetrahedral geometry around each C atom.
- In contrast, the Lewis structures are not meant to imply any 3-D arrangement.

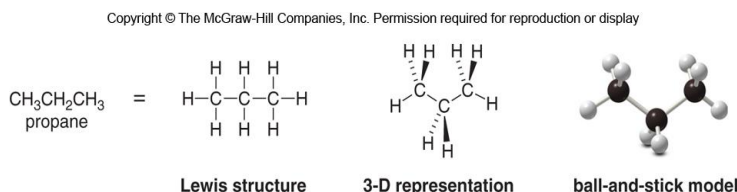
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Drawing Propane

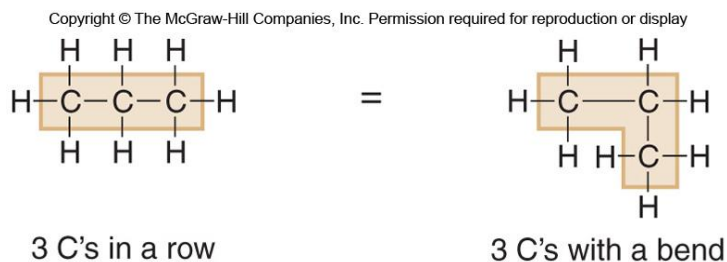
- The three-carbon alkane $\text{CH}_3\text{CH}_2\text{CH}_3$, called propane, has a molecular formula C_3H_8 .
- In the 3-D drawing that each C atom has two bonds in the plane (solid lines), one bond in front (on a wedge) and one bond behind the plane (on a dashed line).



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Equivalent Structures of Propane

- For propane and higher molecular weight alkanes, the carbon skeleton can be drawn in a variety of ways and still represent the same molecule.
- For example, the three carbons of propane can be drawn in a horizontal row or with a bend.
- In a Lewis structure, the bends in a carbon chain do not matter.

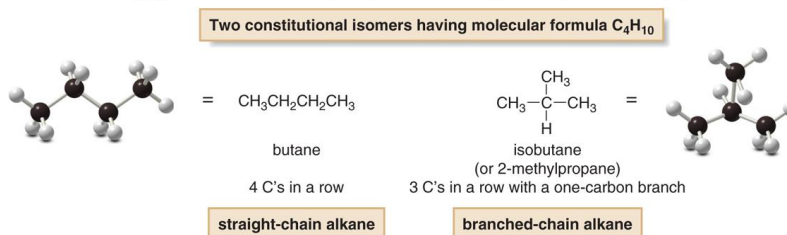


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Constitutional Isomers

- There are two different ways to arrange four carbons, giving two compounds with molecular formula C_4H_{10} , named butane and isobutane.
- Butane and isobutane are **constitutional isomers**—two different compounds with the same molecular formula.
- **Constitutional isomers** (also called **structural isomers**) differ in the way the atoms are connected to each other.

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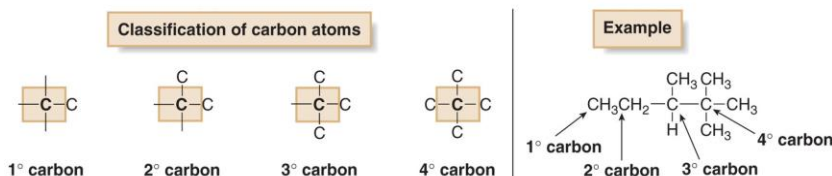


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Classification of Carbon Atoms

- Carbon atoms in alkanes and other organic compounds are classified by the number of other carbons directly bonded to them.
 - A primary (1°) carbon is bonded to one other C atom.
 - A secondary (2°) carbon is bonded to two other C atoms.
 - A tertiary (3°) carbon is bonded to three other C atoms.
 - A quaternary (4°) carbon is bonded to four other C atoms.

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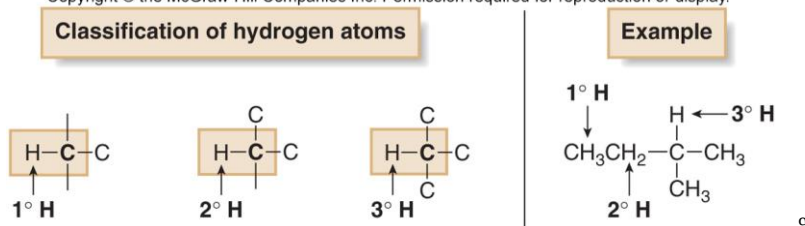


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Classification of Hydrogen Atoms

- Hydrogen atoms are classified depending on the type of carbon atom to which they are bonded.
 - A primary (1°) hydrogen is on a C bonded to one other C atom.
 - A secondary (2°) hydrogen is on a C bonded to two other C atoms.
 - A tertiary (3°) hydrogen is on a C bonded to three other C atoms.

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Naming Alkanes

- The suffix “-ane” identifies a molecule as an alkane.

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Table 4.1 Summary: Straight-Chain Alkanes

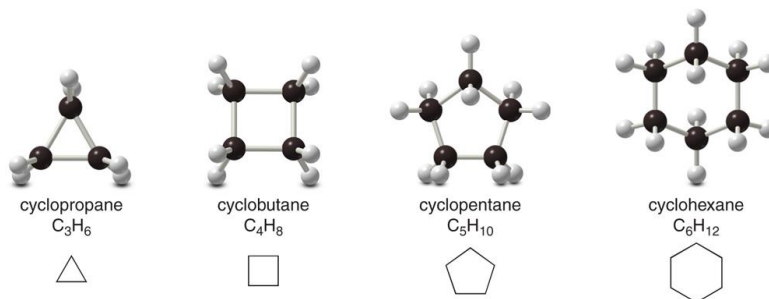
Number of C atoms	Molecular formula	Name (<i>n</i> -alkane)	Number of constitutional isomers	Number of C atoms	Molecular formula	Name (<i>n</i> -alkane)	Number of constitutional isomers
1	CH ₄	methane	—	9	C ₉ H ₂₀	nonane	35
2	C ₂ H ₆	ethane	—	10	C ₁₀ H ₂₂	decane	75
3	C ₃ H ₈	propane	—	11	C ₁₁ H ₂₄	undecane	159
4	C ₄ H ₁₀	butane	2	12	C ₁₂ H ₂₆	dodecane	355
5	C ₅ H ₁₂	pentane	3	13	C ₁₃ H ₂₈	tridecane	802
6	C ₆ H ₁₄	hexane	5	14	C ₁₄ H ₃₀	tetradecane	1858
7	C ₇ H ₁₆	heptane	9	15	C ₁₅ H ₃₂	pentadecane	4347
8	C ₈ H ₁₈	octane	18	20	C ₂₀ H ₄₂	eicosane	366,319

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Cycloalkanes

- **Cycloalkanes** have molecular formula C_nH_{2n} and contain carbon atoms arranged in a ring.
- Simple cycloalkanes are named by adding the prefix **cyclo-** to the name of the acyclic alkane having the same number of carbons.

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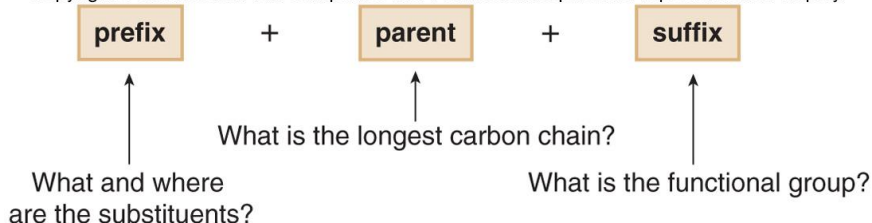
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Nomenclature

The name of every organic molecule has 3 parts:

1. The **parent** name indicates the number of carbons in the longest continuous chain.
2. The **suffix** indicates what functional group is present.
3. The **prefix** tells us the identity, location, and number of substituents attached to the carbon chain.

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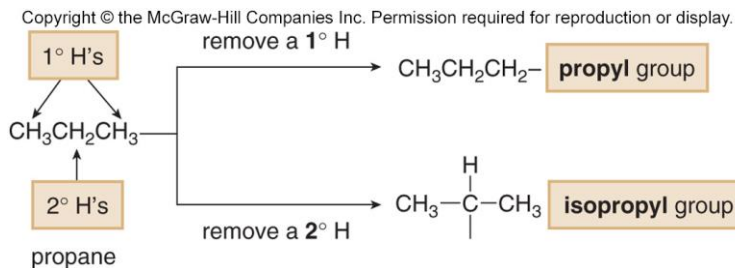
Naming Substituents - Alkyl Groups

- Carbon substituents bonded to a long carbon chain are called **alkyl groups**.
- An alkyl group is formed by **removing one H** atom from an alkane.
- To name an alkyl group, change the **-ane** ending of the parent alkane to **-yl**.
- Thus, methane (CH_4) becomes **methyl** (CH_3 -) and ethane (CH_3CH_3) becomes **ethyl** (CH_3CH_2 -).

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Naming Three Carbon Alkyl Groups

- Naming three- or four-carbon alkyl groups is more complicated because the parent hydrocarbons have **more than one type of hydrogen** atom.
- For example, propane has both **1°** and **2°** H atoms, and removal of each of these H atoms forms a **different alkyl** group with a different name, propyl or isopropyl.

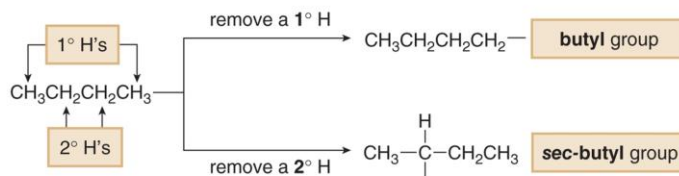


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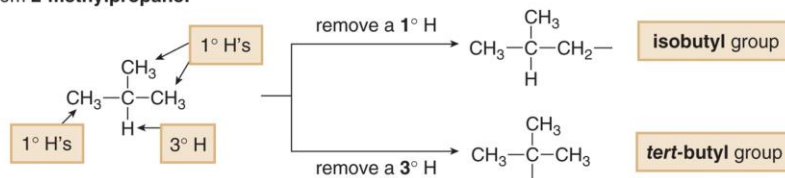
Naming Four Carbon Alkyl Groups

- There are **two different butane** isomers which yield **four** possible **alkyl groups** containing four carbon atoms.

From **butane**:



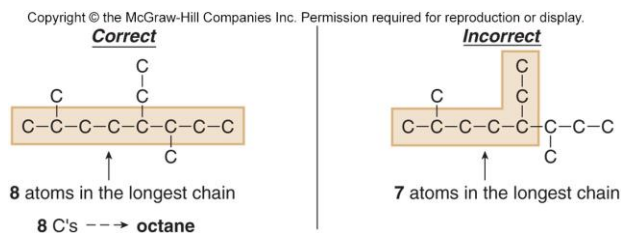
From **2-methylpropane**:



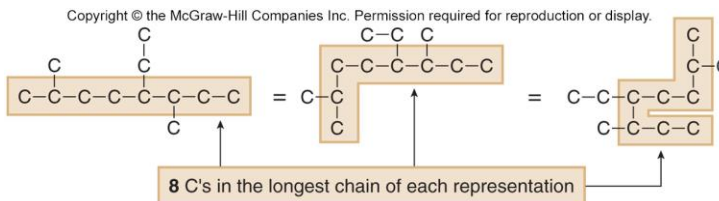
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HOW TO Name an Alkane Using the IUPAC System

Step [1] Find the **parent** (longest continuous) carbon chain and add the suffix.



- It does not matter if the chain is straight or it bends.

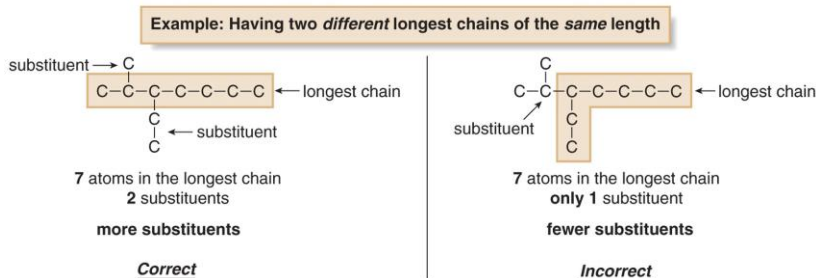


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Naming Structures with Chains of Equal Length

- If there are two chains of equal length, pick the **chain with more substituents**.
- In the following example, two different chains in the same alkane have seven C atoms.
- We circle the longest continuous chain as shown in the diagram on the left, since this results in the greater number of substituents.

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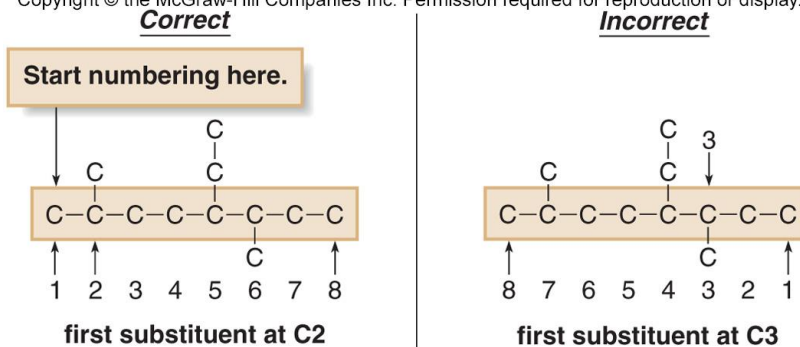


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Numbering Alkanes with Substituents

Step [2] Number the atoms in the carbon chain to give the **first substituent the lowest number**.

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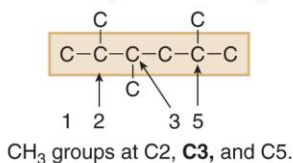
Numbering Substituents

If the **first substituent is the same** distance from both ends, number the chain to give the **second substituent** the lower number.

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Example: Giving a lower number to the *second* substituent

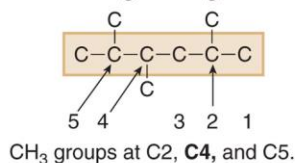
Numbering from *left to right*



The second substituent has a lower number.

Correct

Numbering from *right to left*



higher number

Incorrect

19

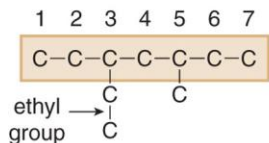
Numbering Substituents

When numbering a carbon chain results in the **same numbers** from either end of the chain, assign the **lower number alphabetically** to the first substituent.

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Example: Two *different* groups *equidistant* from the ends

Numbering from *left to right*

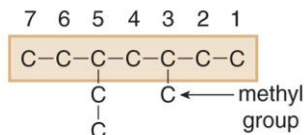


- ethyl at C3
- methyl at C5

Earlier letter → lower number

Correct

Numbering from *right to left*



- methyl at C3
- ethyl at C5

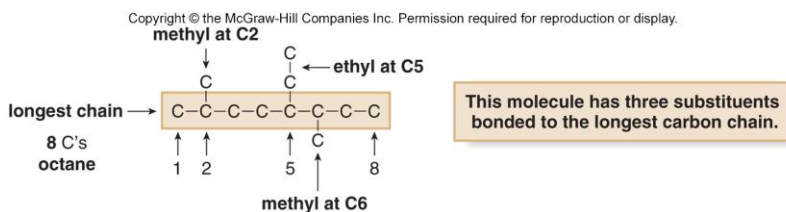
Incorrect

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Naming Substituents

Step [3] Name and number the substituents.

- Name the substituents as alkyl groups.
- Every carbon belongs to either the longest chain or a substituent, not both.
- Each substituent needs its own number.
- If two or more identical substituents are bonded to the longest chain, use **prefixes** to indicate how many: **di-** for two groups, **tri-** for three groups, **tetra-** for four groups, and so forth.

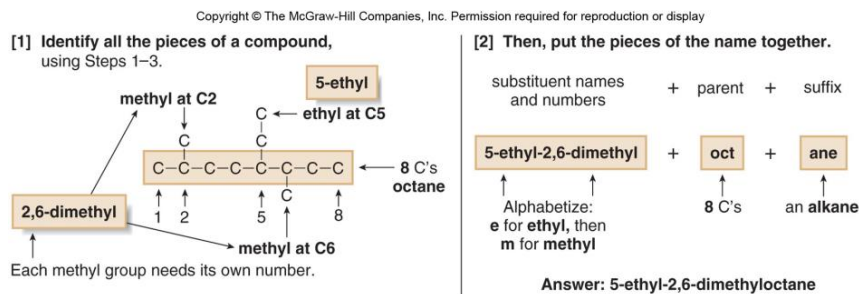


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Completing Structure Names

Step [4] Combine substituent names and numbers + parent + suffix.

- **Precede** the name of the parent by the names of the substituents.
- **Alphabetize** the names of the substituents, ignoring all prefixes except *iso*, as in isopropyl and isobutyl.
- **Precede** the name of each substituent by the number that indicates its location.



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Completing Structure Names

Step [4] cont. Combine substituent names and numbers + parent + suffix.

- **Separate** numbers by commas and separate numbers from letters by hyphens.
- The name of an alkane is a **single word**, with no spaces after hyphens and commas.

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[1] Identify all the pieces of a compound, using Steps 1–3.

[2] Then, put the pieces of the name together.

substituent names and numbers	+	parent	+	suffix
5-ethyl-2,6-dimethyl	+	oct	+	ane
↑ Alphabetize: e for ethyl, then m for methyl		↑ 8 C's		↑ an alkane

Answer: 5-ethyl-2,6-dimethyloctane

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HOW TO Name a Cycloalkane Using the IUPAC System

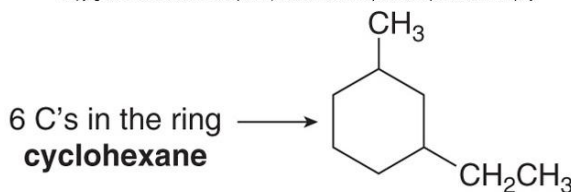
Cycloalkanes are named by using similar rules, but the prefix **cyclo-** immediately precedes the name of the **parent**.

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A ring is present.

prefix	+	cyclo-	+	parent	+	suffix
↑				↑		↑
What and where are the substituents?				How many C's are in the ring?		What is the functional group?

Step [1] Find the parent cycloalkane.

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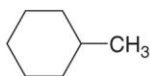


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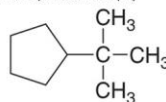
Numbering Substituents in Cycloalkanes

Step [2] Name and number the substituents. No number is needed to indicate the location of a **single substituent**.

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methylcyclohexane

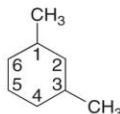


tert-butylcyclopentane

For rings with more than one substituent, begin numbering at one substituent and proceed around the ring to give the second substituent the **lowest number**.

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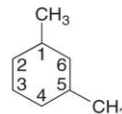
numbering clockwise



CH₃ groups at C1 and C3
The 2nd substituent has a lower number.

Correct: 1,3-dimethylcyclohexane

numbering counterclockwise



CH₃ groups at C1 and C5

Incorrect: 1,5-dimethylcyclohexane

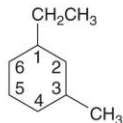
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Naming Cycloalkane Substituents Alphabetically

With **two different substituents**, number the ring to assign the lower number to the substituents **alphabetically**.

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Begin numbering at the ethyl group.

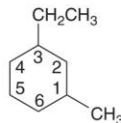


- ethyl group at C1
- methyl group at C3

earlier letter → lower number

Correct: 1-ethyl-3-methylcyclohexane

Begin numbering at the methyl group.



- methyl group at C1
- ethyl group at C3

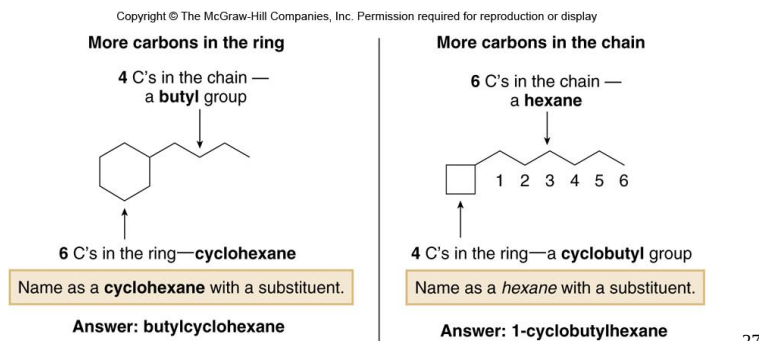
Incorrect: 3-ethyl-1-methylcyclohexane

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Naming Alkanes vs. Cycloalkanes

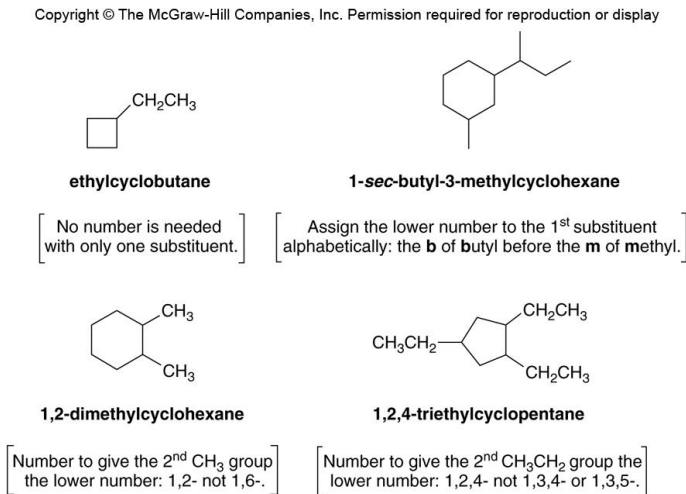
- If the number of carbons in the ring is **greater than or equal** to the number of carbons in the longest chain, the compound is named as a cycloalkane.
- If there are more carbons in the chain, the compound is named as an alkane.

Figure 4.2



Examples of Naming Cycloalkanes

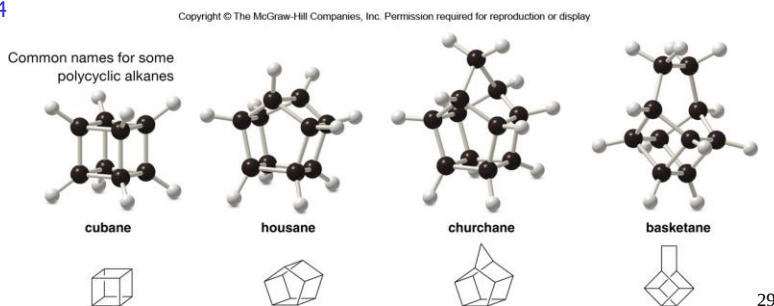
Figure 4.3



Common Names of Polycyclic Molecules

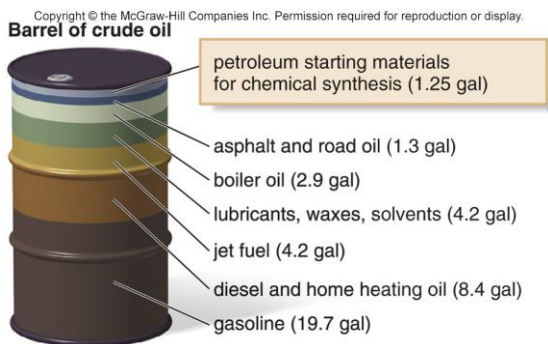
- Some organic compounds are identified using common names that **do not follow the IUPAC** system of nomenclature.
- Many of these names were given long ago before the IUPAC system was adopted, and are still widely used.
- Additionally, some names are **descriptive of shape** and structure, like those below:

Figure 4.4



Fossil Fuels

- Many alkanes occur in nature, primarily in natural gas and petroleum.
- **Natural gas** is composed largely of **methane**, with lesser amounts of ethane, propane, and butane.
- **Petroleum** is a complex mixture of compounds, most of which are hydrocarbons containing **one to forty carbon** atoms.



Refining of Oil

- **Distilling** crude petroleum (called refining), separates it into usable fractions that differ in boiling point.

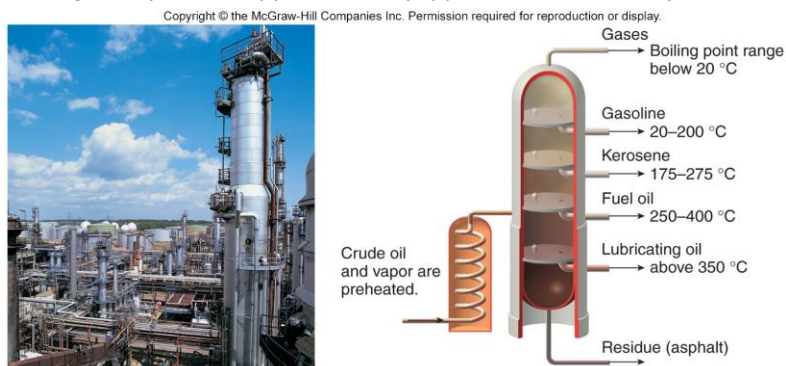
gasoline: $C_5H_{12}-C_{12}H_{26}$

kerosene: $C_{12}H_{26}-C_{16}H_{34}$

diesel fuel: $C_{15}H_{32}-C_{18}H_{38}$

Figure 4.5

Refining crude petroleum. (a) An oil refinery. (b) Schematic of a refinery tower.



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Properties of Alkanes

- Alkanes contain only **nonpolar** C—C and C—H bonds.
 - They only exhibit weak **van der Waals** forces.
 - This affects solubility and boiling point and melting point characteristics of alkanes.
- Solubility of alkanes
 - Alkanes are **soluble** in **organic solvents**.
 - Alkanes are insoluble in water.

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Properties of Alkanes

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Table 4.2 Physical Properties of Alkanes

Property	Observation
Boiling point and melting point	- Alkanes have low bp's and mp's compared to more polar compounds of comparable size. $\text{CH}_3\text{CH}_2\text{CH}_3$ VDW bp = -42°C mp = -190°C CH_3CHO VDW, DD bp = 21°C mp = -121°C  Increasing strength of intermolecular forces Increasing boiling point and melting point - Bp and mp increase as the number of carbons increases because of increased surface area. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ bp = 0°C mp = -138°C $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ bp = 69°C mp = -95°C  Increasing surface area Increasing boiling point and melting point - The bp of isomers decreases with branching because of decreased surface area. $(\text{CH}_3)_4\text{C}$ bp = 10°C $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ bp = 30°C $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ bp = 36°C  Increasing surface area Increasing boiling point - Mp increases with increased symmetry. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$ mp = -160°C $(\text{CH}_3)_4\text{C}$ mp = -17°C  Increasing symmetry Increasing melting point
Solubility	- Alkanes are soluble in organic solvents. - Alkanes are insoluble in water.

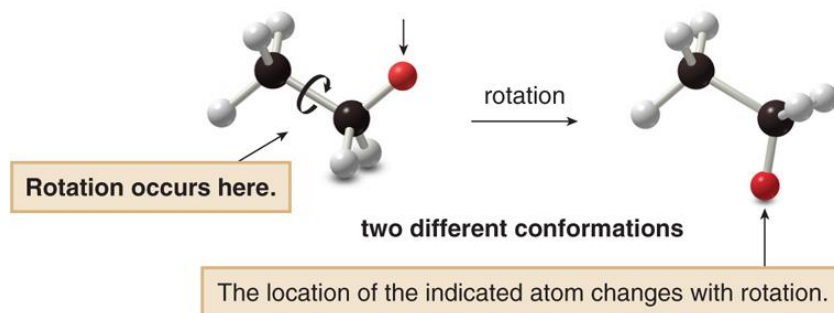
Key: bp = boiling point; mp = melting point; VDW = van der Waals; DD = dipole-dipole; HB = hydrogen bonding

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Conformations of Acyclic Alkanes

Conformations are different arrangements of atoms that are interconverted by rotation about single bonds.

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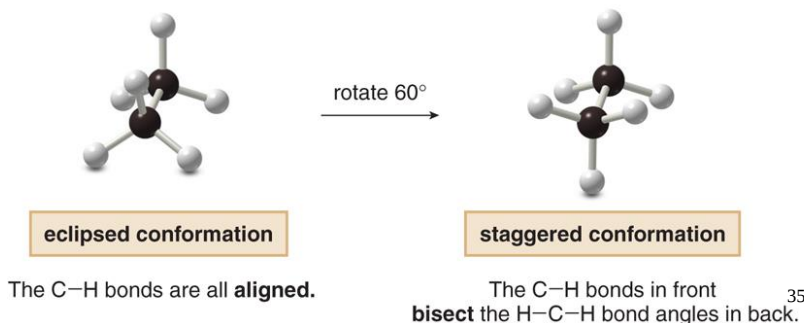


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Eclipsed and Staggered Conformations

- Names are given to two different conformations.
- In the **eclipsed** conformation, the C-H bonds on one carbon are directly aligned with the C-H bonds on the adjacent carbon.
- In the **staggered** conformation, the C-H bonds on one carbon bisect the H-C-H bond angle on the adjacent carbon.

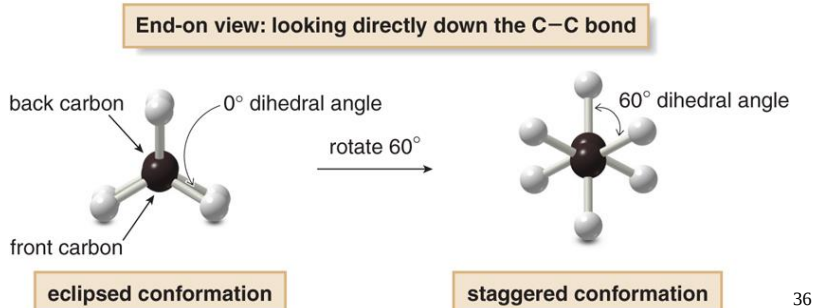
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Conformations and Dihedral Angle

- Rotating the atoms on one carbon by 60° converts an eclipsed conformation into a staggered conformation, and vice versa.
- The angle that separates a bond on one atom from a bond on an adjacent atom is called a **dihedral angle**.
- For ethane in the staggered conformation, the dihedral angle for the C-H bonds is 60° ; for eclipsed ethane, it is 0° .

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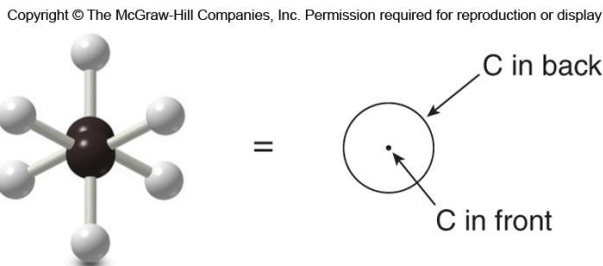
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Newman Projections

- End-on representations for conformations are commonly drawn using a convention called a **Newman projection**.

HOW TO Draw a Newman Projection:

Step [1] Look directly down the C-C bond (end-on), and draw a circle with a dot in the center to represent the carbons of the C-C bond.

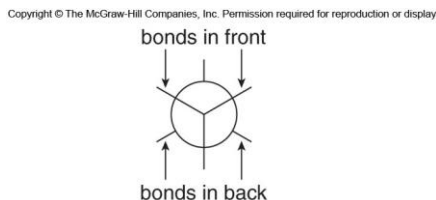


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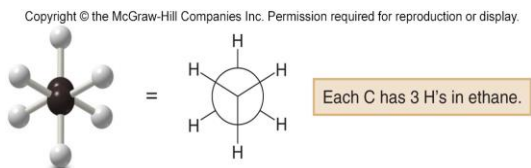
Completing a Newman Projection

Step 2. Draw in the bonds.

- Draw the bonds on the front C as three lines meeting at the center of the circle.
- Draw the bonds on the back C as three lines coming out of the edge of the circle.



Step 3. Add the atoms on each bond.

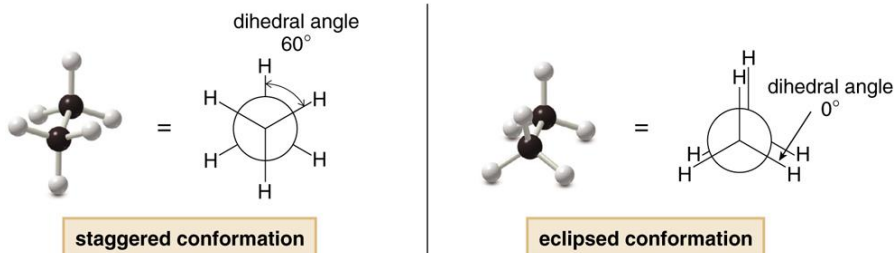


38

Newman Projections - Ethane

Figure 4.6

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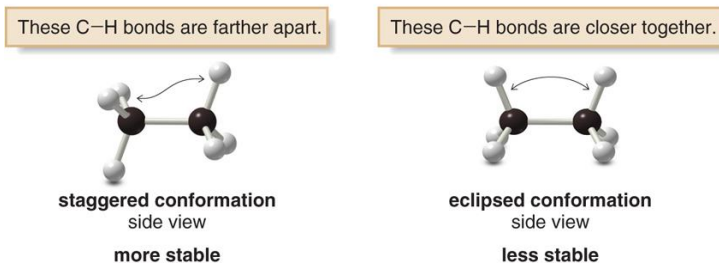


39

Conformations of Ethane

- The staggered and eclipsed conformations of ethane interconvert at room temperature.
- The staggered conformations are more stable (lower in energy) than the eclipsed conformations.
- Electron-electron repulsion between bonds in the eclipsed conformation increases its energy compared with the staggered conformation, where the bonding electrons are farther apart.

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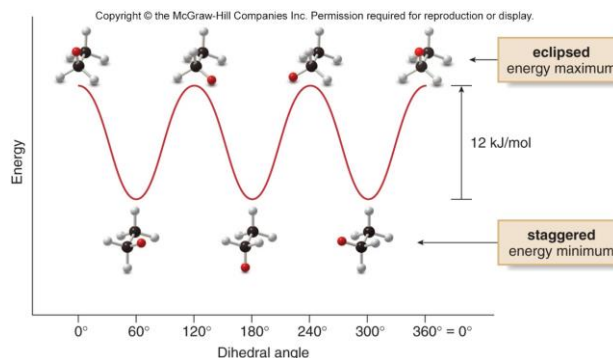


40

Torsional Energy of Ethane

- The difference in energy between staggered and eclipsed conformers is ~ 3 kcal/mol, with each eclipsed C-H bond contributing 1 kcal/mol.
- The energy difference between staggered and eclipsed conformers is called **torsional energy**.
- **Torsional strain** is an increase in energy caused by eclipsing interactions.

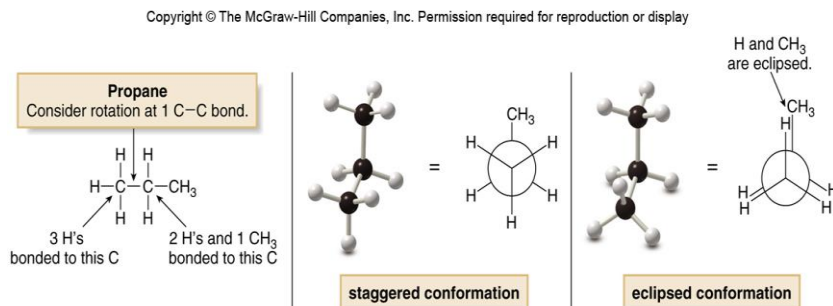
Figure 4.8



41

Newman Projections - Propane

Figure 4.7

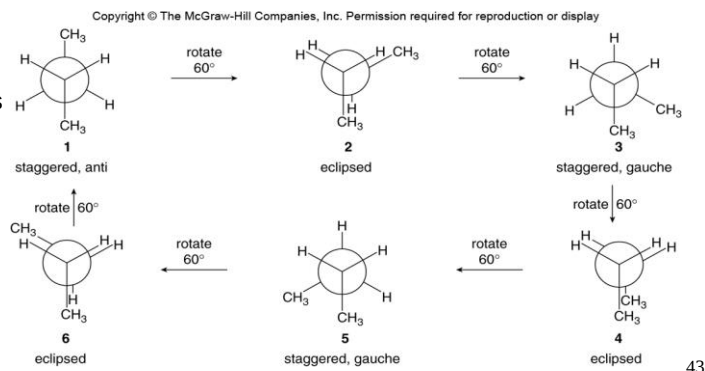


42

Newman Projections - Butane

- An energy minimum and maximum occur every 60° as the conformation changes from staggered to eclipsed.
- Conformations that are neither staggered nor eclipsed are intermediate in energy.
- Butane and higher molecular weight alkanes have several C-C bonds, all capable of rotation.

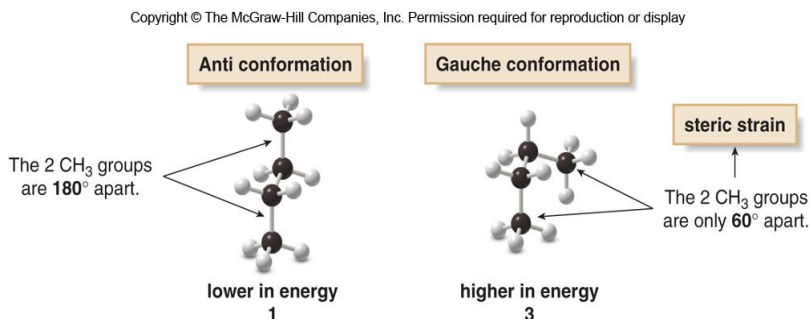
Figure 4.9
Six different conformations of butane



43

Anti and Gauche Conformations

- A staggered conformation with two larger groups 180° from each other is called **anti**.
- A staggered conformation with two larger groups 60° from each other is called **gauche**.
- The staggered conformations are lower in energy than the eclipsed conformations.



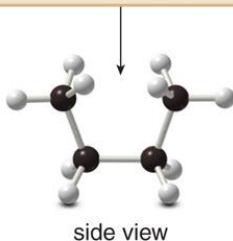
44

Steric Strain

- The relative energies of the individual staggered conformations depend on their steric strain.
- **Steric strain** is an increase in energy resulting when non-bonded atoms are forced too close to one another.
- Gauche conformations are generally higher in energy than anti conformations because of steric strain.

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Steric strain caused by two eclipsed CH₃ groups

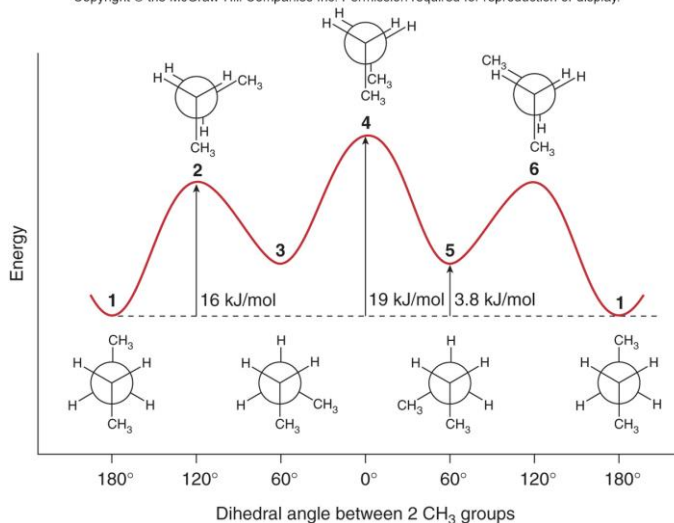


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Conformation and Energy of Butane

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Figure 4.10



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Barrier to Rotation

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Table 4.3 Summary: Torsional and Steric Strain Energies in Acyclic Alkanes

Type of interaction	Energy increase	
	kJ/mol	kcal/mol
H,H eclipsing	4.0	1.0
H,CH ₃ eclipsing	6.0	1.4
CH ₃ ,CH ₃ eclipsing	11	2.6
gauche CH ₃ groups	3.8	0.9

- The energy difference between the lowest and highest energy conformations is called a **barrier to rotation**.

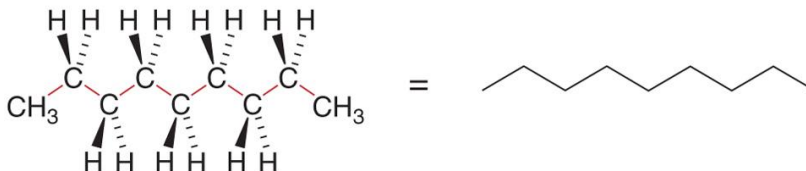
47

Zigzag Skeletal Structures

- Since the lowest energy conformation has all bonds staggered and all large groups anti, alkanes are often drawn in zigzag skeletal structures to indicate this.

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A zigzag arrangement keeps all carbons **staggered** and **anti**.



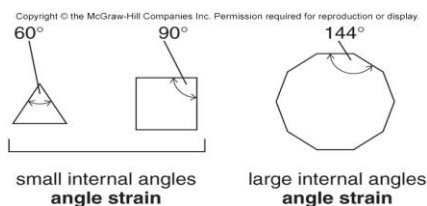
48

Angle Strain in Cycloalkanes

- Besides torsional strain and steric strain, the conformations of cycloalkanes are also affected by angle strain.
- **Angle strain** is an increase in energy when bond angles deviate from the optimum tetrahedral angle of 109.5° .
- Cycloalkanes with more than three C atoms in the ring are not flat molecules. They are puckered to reduce strain.

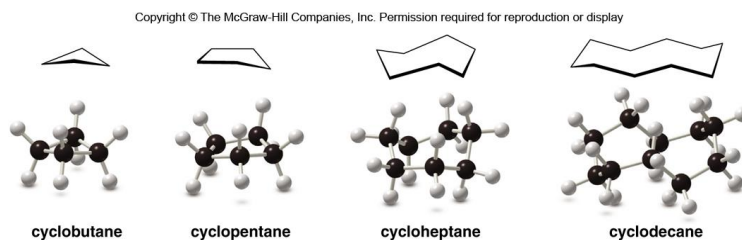
49

Three to Ten Carbon Cycloalkanes



Cycloalkanes distort their shapes to alleviate angle and torsional strain.

Figure 4.11

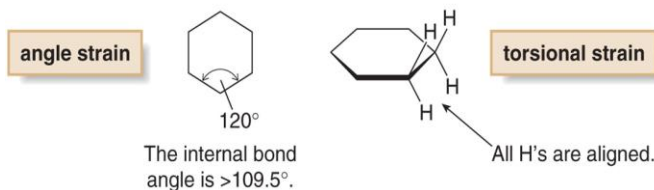


50

Cyclohexane

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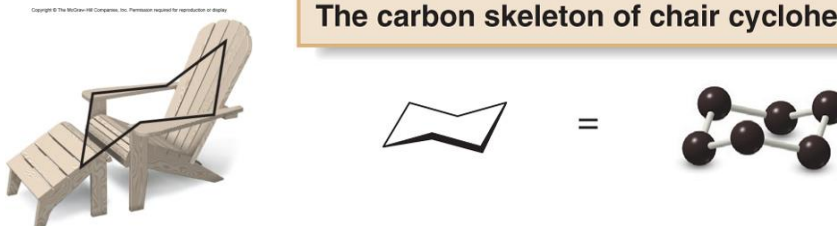
If a cyclohexane ring were flat....



- In reality, cyclohexane adopts a puckered “chair” conformation, which is more stable than any other possible conformation.

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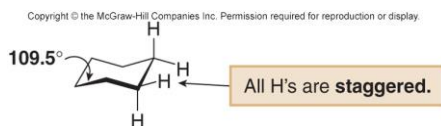
The carbon skeleton of chair cyclohexane



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Chair Conformation

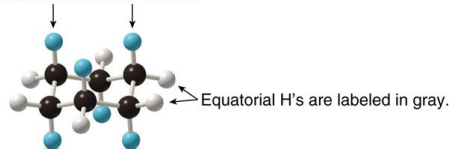
- The chair conformation is so stable because it eliminates angle strain (all C-C-C angles are 109.5°), and torsional strain (all hydrogens on adjacent C atoms are staggered).



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Axial H's are labeled in blue.

Figure 4.12



- Cyclohexane has six axial H's and six equatorial H's.

- In cyclohexane, three C atoms pucker up and three C atoms pucker down, alternating around the ring.

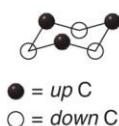
52

Axial and Equatorial Positions

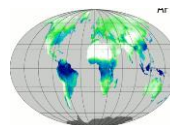
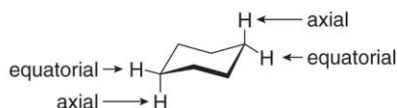
- Each C in cyclohexane has two different kinds of hydrogens:
 - Axial** hydrogens are located above and below the ring (along a perpendicular axis).
 - Equatorial** hydrogens are located in the plane of the ring (around the equator).

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3 up C's and 3 down C's



Two kinds of H's



- Axial** bonds are oriented **above** and **below**.
- Equatorial** bonds are oriented around the **equator**.

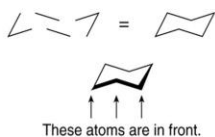
53

Drawing Cyclohexanes

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HOW TO Draw the Chair Form of Cyclohexane

Step [1] Draw the carbon skeleton.

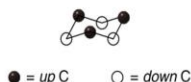


- Draw three parts of the chair: **a wedge, a set of parallel lines, and another wedge.**
- Then, join them together.
- The bottom 3 C's come out of the page, and for this reason, bonds to them are often highlighted in bold.

HOW TO, continued . . .

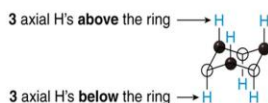
—Continued

Step [2] Label the *up* C's and *down* C's on the ring.



- There are 3 *up* and 3 *down* C's, and they alternate around the ring.

Step [3] Draw in the axial H atoms.



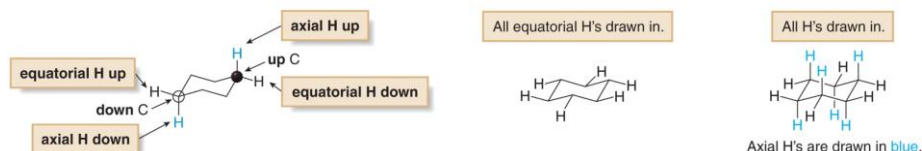
- On an *up* C the axial H is *up*.
- On a *down* C the axial H is *down*.

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Drawing Hydrogens on Cyclohexanes

Step [4] Draw in the equatorial H atoms. Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display

- The axial H is **down** on a down C, so the equatorial H must be up.
- The axial H is **up** on an up C, so the equatorial H must be down.



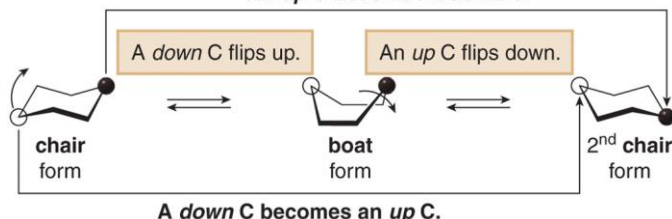
55

Conformational Change – Ring-Flipping

- Cyclohexanes undergo a conformational change called “**ring-flipping**.”
- As a result of a ring flip, the up carbons become down carbons, and the down carbons become up carbons.
- Axial and equatorial H atoms are also interconverted during a ring-flip; axial H atoms become equatorial H atoms, and equatorial H atoms become axial H atoms.

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An up C becomes a down C.



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Conformational Change – Ring-Flipping

- There are two possible chair conformations.
- The equatorial position has more room than the axial position, so larger substituents are more stable in the equatorial position.

Figure 4.13



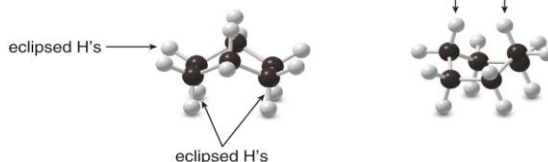
57

Boat Conformation of Cyclohexane

- Cyclohexane also can exist in a boat conformation.
- The boat forms of cyclohexane are 7 kcal/mol less stable than the chair forms.
- The **boat conformation** is destabilized by torsional strain because the hydrogens on the four carbon atoms in the plane are eclipsed.
- Additionally, there is steric strain because two hydrogens at either end of the boat, the “**flag pole**” hydrogens, are forced close to each other.

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Figure 4.14



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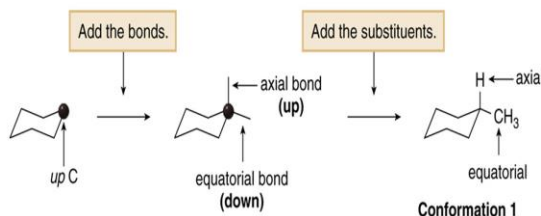
Drawing Substituted Cyclohexanes

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HOW TO Draw the Two Conformations for a Substituted Cyclohexane

Step [1] Draw one chair form and add the substituents.

- Arbitrarily pick a ring carbon, classify it as an *up* or *down* carbon, and draw the bonds. Each C has one axial and one equatorial bond.
- Add the substituents, in this case H and CH₃, arbitrarily placing one axial and one equatorial. In this example, the CH₃ group is drawn equatorial.
- This forms one of the two possible chair conformations, labeled Conformation 1.

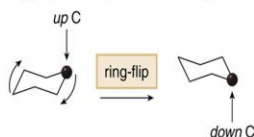


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HOW TO Draw the Two Conformations for a Substituted Cyclohexane

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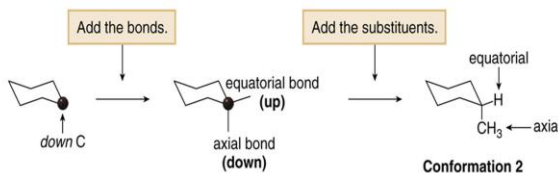
Step [2] Ring-flip the cyclohexane ring.



- Convert *up* C's to *down* C's and vice versa. The chosen *up* C now puckers down.

Step [3] Add the substituents to the second conformation.

- Draw axial and equatorial bonds. On a *down* C the axial bond is *down*.
- Ring-flipping converts axial bonds to equatorial bonds, and vice versa. The equatorial methyl becomes axial.
- This forms the other possible chair conformation, labeled Conformation 2.

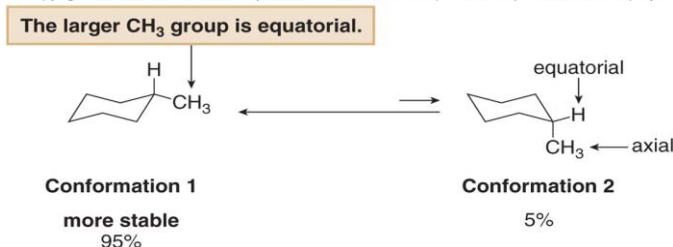


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Chair Conformations and Energy

- The two chair conformations of cyclohexane are different, so they are not equally stable.
- Larger axial substituents create destabilizing (and thus unfavorable) **1,3-diaxial interactions**.
- In methylcyclohexane, each unfavorable H,CH₃ interaction destabilizes the conformation by 0.9 kcal/mol, so Conformation 2 is 1.8 kcal/mol less stable than Conformation 1.

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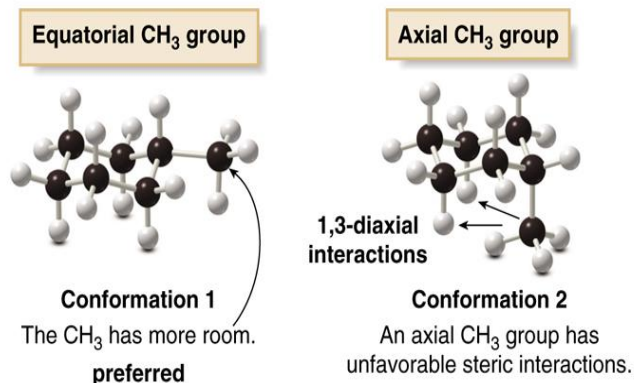
61

Preference of Equatorial Position in Substituted Cyclohexanes

- Three dimensional representations for the two chair conformations of methylcyclohexane.

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Figure 4.15

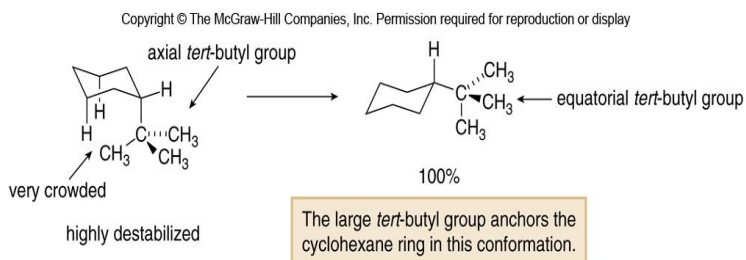


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Preference of Equatorial Position in Substituted Cyclohexanes

- The larger the substituent on the six-membered ring, the higher the percentage of the equatorial conformation at equilibrium.
- With a very large substituent like *tert*-butyl $[(\text{CH}_3)_3\text{C}-]$, essentially none of the conformation containing an axial *tert*-butyl group is present at room temperature.

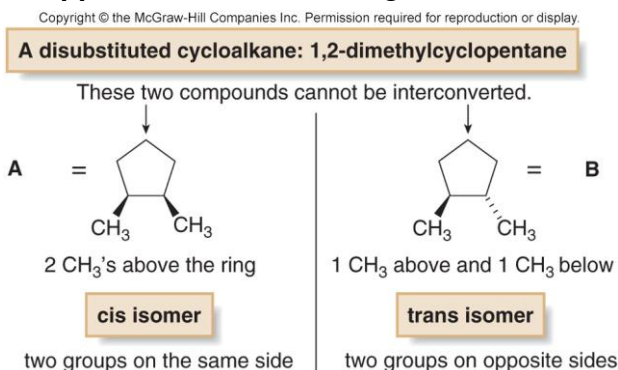
Figure 4.16



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Disubstituted Cycloalkanes

- There are two different 1,2-dimethylcyclopentanes—one having two CH_3 groups on the same side of the ring and one having them on opposite sides of the ring.



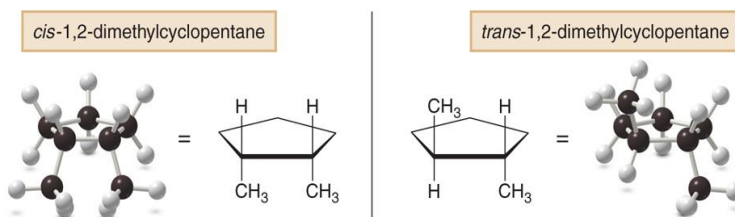
- A and B are stereoisomers.

64

Cis and Trans Stereoisomers

- Stereoisomers are isomers that differ only in the way the atoms are oriented in space.
- The prefixes **cis** and **trans** are used to distinguish these isomers.
- The cis isomer has two groups on the same side of the ring.
- The trans isomer has two groups on opposite sides of the ring.

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Disubstituted Cycloalkanes

- A disubstituted cyclohexane, such as 1,4-dimethylcyclohexane, also has cis and trans stereoisomers.
- Each of these stereoisomers has two possible chair conformations.

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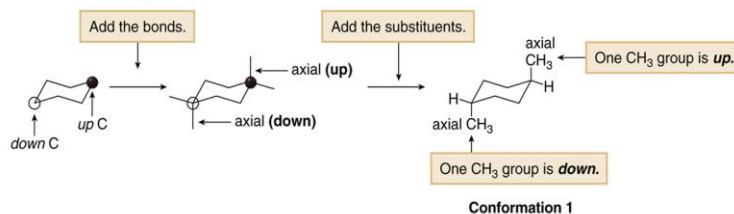
Drawing Disubstituted Cyclohexanes

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HOW TO Draw Two Conformations for a Disubstituted Cyclohexane

Step [1] Draw one chair form and add the substituents.

- For *trans*-1,4-dimethylcyclohexane, arbitrarily pick two C's located 1,4- to each other, classify them as *up* or *down* C's, and draw in the substituents.
- The *trans* isomer must have one group *above* the ring (on an *up* bond) and one group *below* the ring (on a *down* bond). The substituents can be either axial or equatorial, as long as one is up and one is down. The easiest *trans* isomer to visualize has two axial CH₃ groups. This arrangement is said to be **diaxial**.
- This forms one of the two possible chair conformations, labeled Conformation 1.

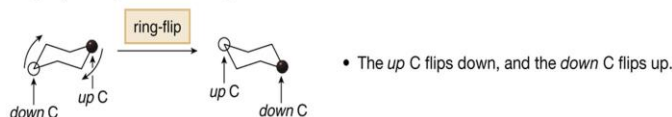


67

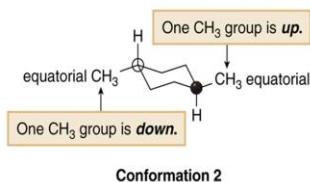
Drawing the Second Conformation of Cyclohexanes

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Step [2] Ring-flip the cyclohexane ring.



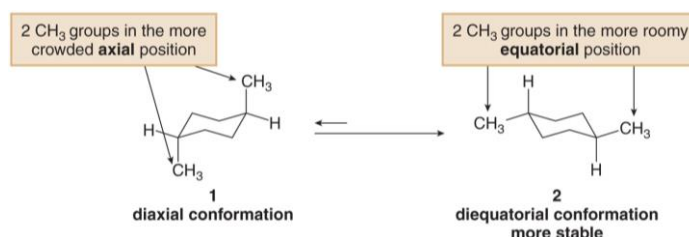
Step [3] Add the substituents to the second conformation.



- Ring-flipping converts axial bonds to equatorial bonds, and vice versa. The diaxial CH₃ groups become diequatorial. This *trans* conformation is less obvious to visualize. It is still *trans*, because one CH₃ group is above the ring (on an *up* bond), and one is below (on a *down* bond).

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Trans Disubstituted Cycloalkanes



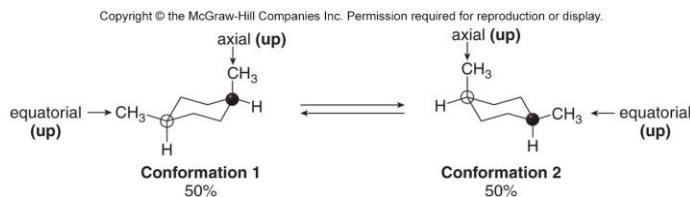
- Conformations 1 and 2 are not equally stable.
- Because conformation 2 has both CH_3 groups in the roomier equatorial position, it is lower in energy.
- A trans isomer has two substituents on opposite sides, one up and one down.

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Cis Disubstituted Cycloalkanes

- A cis isomer has two groups on the same side of the ring, either both *up* or both *down*.
- In this example, Conformations 1 and 2 have two CH_3 groups drawn *up*.
- Both conformations have one CH_3 group axial and one equatorial, making them equally stable.

Figure 4.17



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Cellulose vs Starch

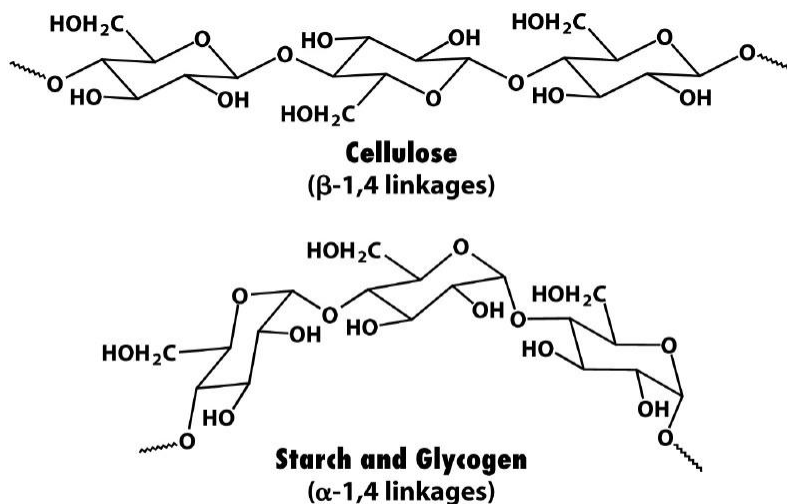


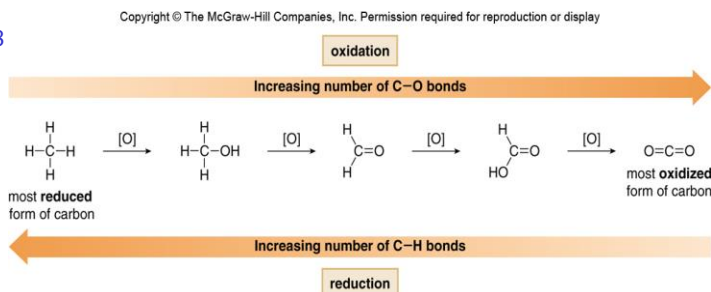
Figure 11-14
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Oxidation and Reduction Reactions

- Oxidation results in an increase in the number of C-Z bonds.
- Oxidation results in a decrease in the number of C-H bonds.
- Reduction results in a decrease in the number of C-Z bonds.
- Reduction results in an increase in the number of C-H bonds.

Figure 4.18

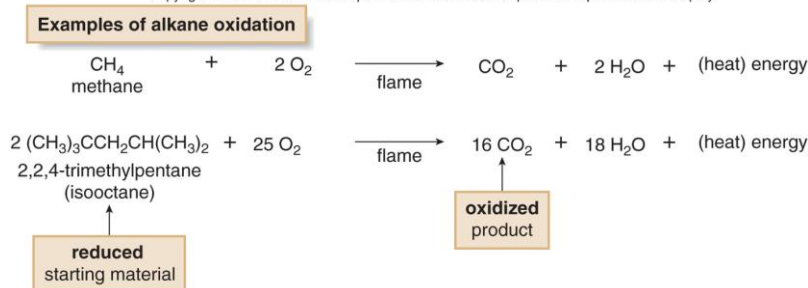


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Combustion of Alkanes

- Alkanes undergo combustion — that is, they burn in the presence of oxygen to form carbon dioxide and water.
- This is an example of an oxidation-reduction reaction. Every C-H and C-C bond in the starting material is converted to a C-O bond in the product.

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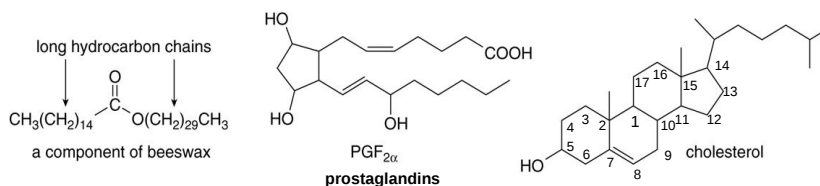
73

Lipids

- Lipids are biomolecules that are soluble in organic solvents and insoluble in water.
- Lipids are composed of many nonpolar C-H and C-C bonds, and have few polar functional groups.
- The metabolism of lipids provides energy for our bodies.

Figure 4.20 Three representative lipid molecules

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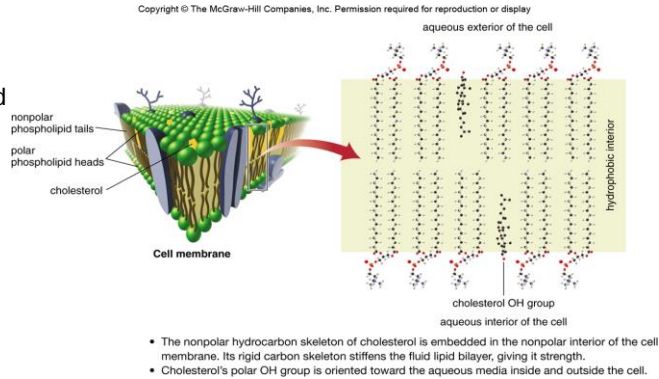
74

Cholesterol

- Cholesterol is a member of the steroid family, a group of lipids having four rings joined together.
- Because it has just one polar OH group, it is insoluble in the aqueous medium of the blood.

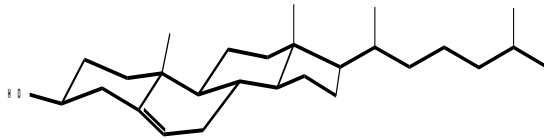
Figure 4.21

Cholesterol embedded in a lipid bilayer of a cell membrane



75

Cholesterol



76