

# Organic Chemistry, *Fourth Edition*

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## Chapter 4 Alkanes (Acyclic Alkanes and Cycloalkanes)

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### Acyclic Alkanes

- Alkanes are aliphatic hydrocarbons having only C-C and C-H  $\sigma$  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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An acyclic alkane



undecane  
 $C_{11}H_{24}$

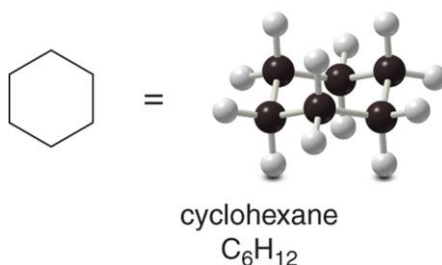
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# Cycloalkanes

- **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

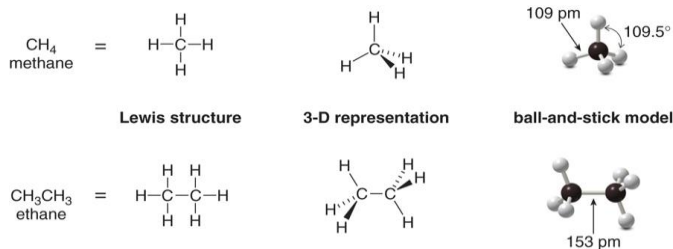


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## Tetrahedral Geometry of Carbon

- All C atoms in an alkane are surrounded by four groups, making them  $sp^3$  hybridized and tetrahedral, with all bond angles of  $109.5^\circ$ .
- 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.

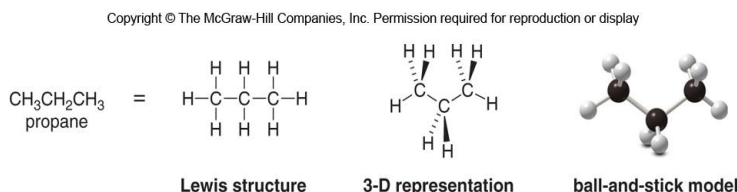
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## Drawing Propane

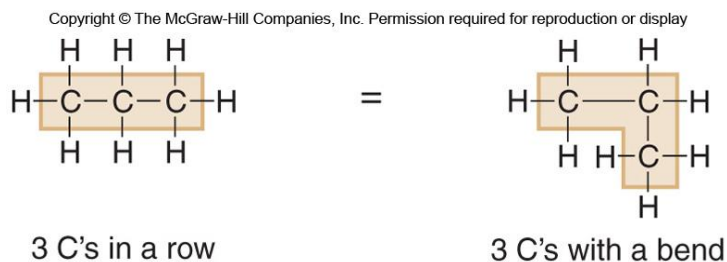
- The three-carbon alkane  $\text{CH}_3\text{CH}_2\text{CH}_3$ , called propane, has a molecular formula  $\text{C}_3\text{H}_8$ .
- In the 3-D drawing that each C atom has two bonds in the plane (solid lines), one bond in front (on a wedge) and one bond behind the plane (on a dashed line).



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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.

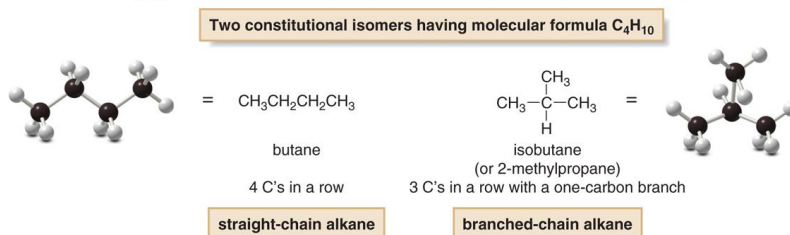


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## Constitutional Isomers

- 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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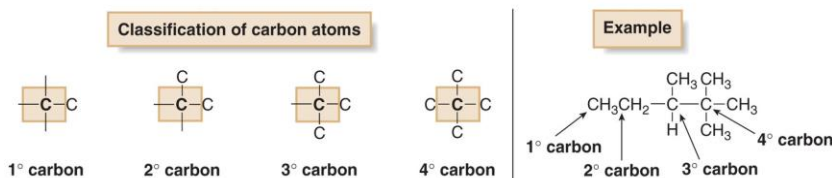


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## Classification of Carbon Atoms

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

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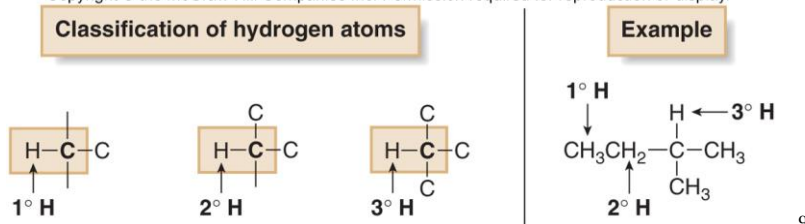


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## Classification of Hydrogen Atoms

- Hydrogen atoms are classified depending on the type of carbon atom to which they are bonded.
  - A primary ( $1^\circ$ ) hydrogen is on a C bonded to one other C atom.
  - A secondary ( $2^\circ$ ) hydrogen is on a C bonded to two other C atoms.
  - A tertiary ( $3^\circ$ ) 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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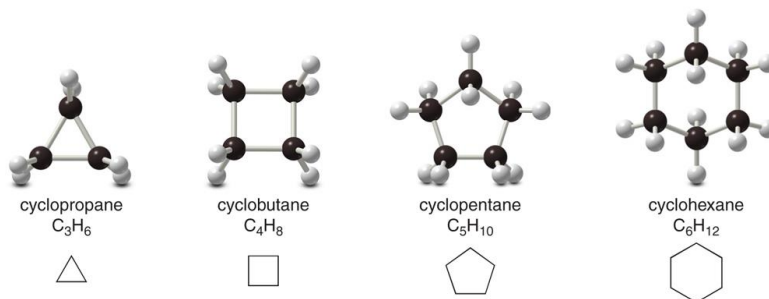
Table 4.1 Summary: Straight-Chain Alkanes

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 <sub>4</sub>	methane	—	9	C <sub>9</sub> H <sub>20</sub>	nonane	35
2	C <sub>2</sub> H <sub>6</sub>	ethane	—	10	C <sub>10</sub> H <sub>22</sub>	decane	75
3	C <sub>3</sub> H <sub>8</sub>	propane	—	11	C <sub>11</sub> H <sub>24</sub>	undecane	159
4	C <sub>4</sub> H <sub>10</sub>	butane	2	12	C <sub>12</sub> H <sub>26</sub>	dodecane	355
5	C <sub>5</sub> H <sub>12</sub>	pentane	3	13	C <sub>13</sub> H <sub>28</sub>	tridecane	802
6	C <sub>6</sub> H <sub>14</sub>	hexane	5	14	C <sub>14</sub> H <sub>30</sub>	tetradecane	1858
7	C <sub>7</sub> H <sub>16</sub>	heptane	9	15	C <sub>15</sub> H <sub>32</sub>	pentadecane	4347
8	C <sub>8</sub> H <sub>18</sub>	octane	18	20	C <sub>20</sub> H <sub>42</sub>	eicosane	366,319

# 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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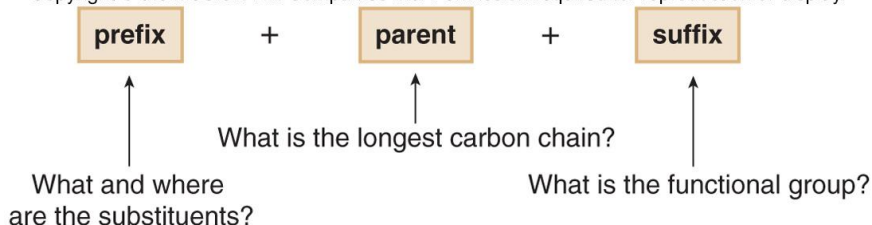
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# Nomenclature

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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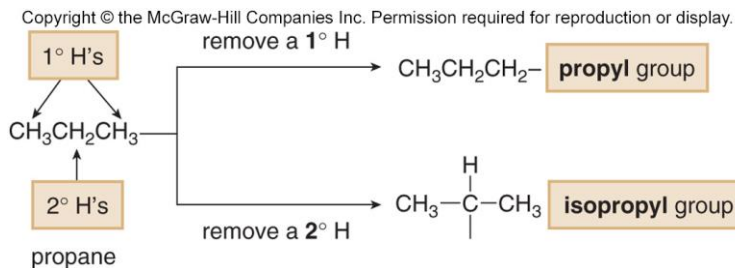
## Naming Substituents - Alkyl Groups

- 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<sub>4</sub>) becomes **methyl** (CH<sub>3</sub>-) and ethane (CH<sub>3</sub>CH<sub>3</sub>) becomes **ethyl** (CH<sub>3</sub>CH<sub>2</sub>-).

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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.

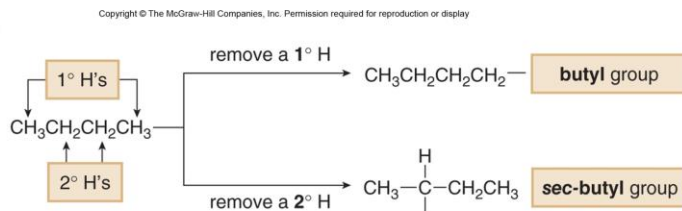


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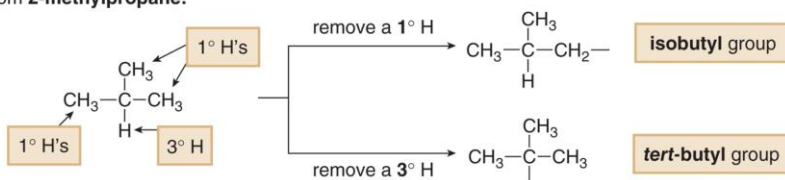
## Naming Four Carbon Alkyl Groups

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

From **butane**:



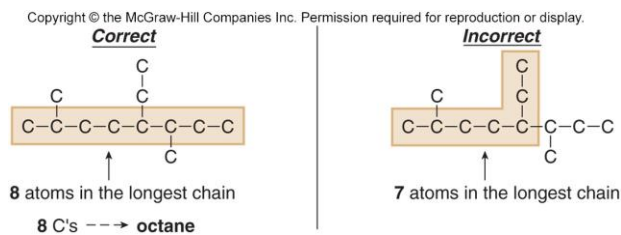
From **2-methylpropane**:



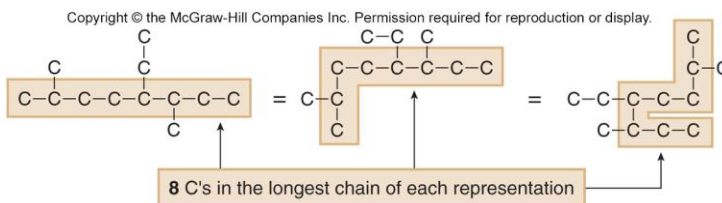
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## HOW TO Name an Alkane Using the IUPAC System

- 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.



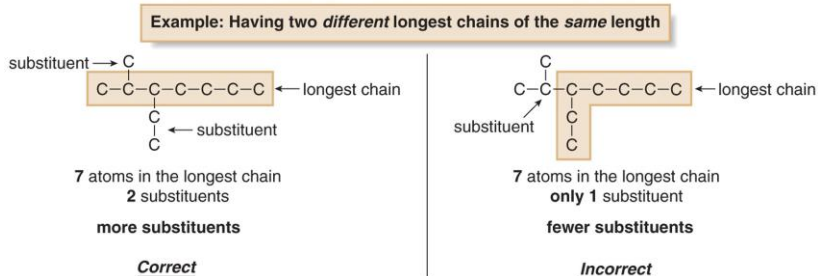
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## Naming Structures with Chains of Equal Length

- 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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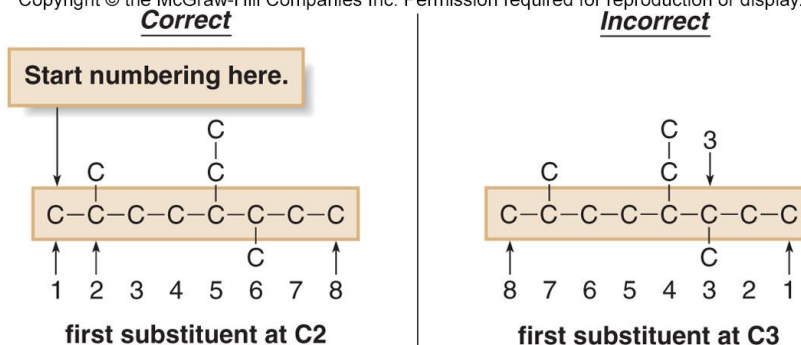


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## Numbering Alkanes with Substituents

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

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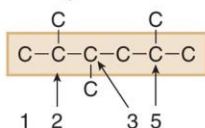
## Numbering Substituents

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*

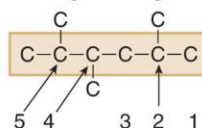


CH<sub>3</sub> groups at C2, **C3**, and C5.

The second substituent has a lower number.

Correct

Numbering from *right to left*



CH<sub>3</sub> groups at C2, **C4**, and C5.

higher number

Incorrect

19

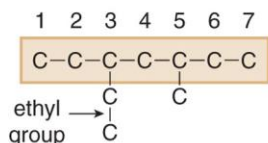
## Numbering Substituents

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*

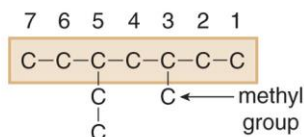


- ethyl at C3
- methyl at C5

Earlier letter → lower number

Correct

Numbering from *right to left*



- methyl at C3
- ethyl at C5

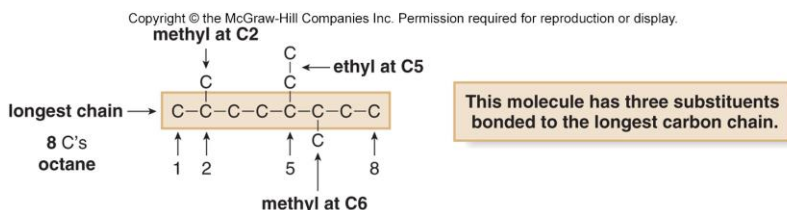
Incorrect

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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.

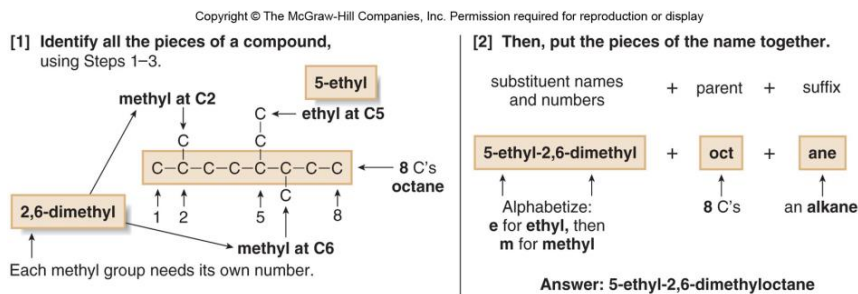


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# Completing Structure Names

**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.

Diagram showing the identification of substituents and parent chain for 5-ethyl-2,6-dimethyloctane. The parent chain is an 8-carbon octane chain. Substituents include an ethyl group at C5 and two methyl groups at C2 and C6. The parent chain is labeled "8 C's octane".

[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

Each methyl group needs its own number.

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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**.

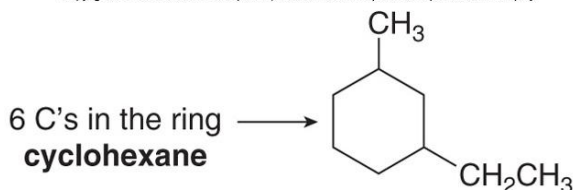
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A ring is present.

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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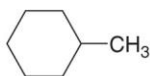


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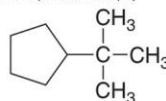
# Numbering Substituents in Cycloalkanes

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

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methylcyclohexane

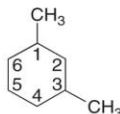


tert-butylcyclopentane

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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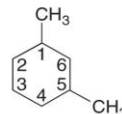
**numbering clockwise**



CH<sub>3</sub> groups at C1 and C3  
The 2<sup>nd</sup> substituent has a lower number.

**Correct:** 1,3-dimethylcyclohexane

**numbering counterclockwise**



CH<sub>3</sub> groups at C1 and C5

**Incorrect:** 1,5-dimethylcyclohexane

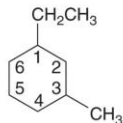
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## Naming Cycloalkane Substituents Alphabetically

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.**

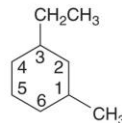


- ethyl group at C1
- methyl group at C3

earlier letter → lower number

**Correct:** 1-ethyl-3-methylcyclohexane

**Begin numbering at the methyl group.**



- methyl group at C1
- ethyl group at C3

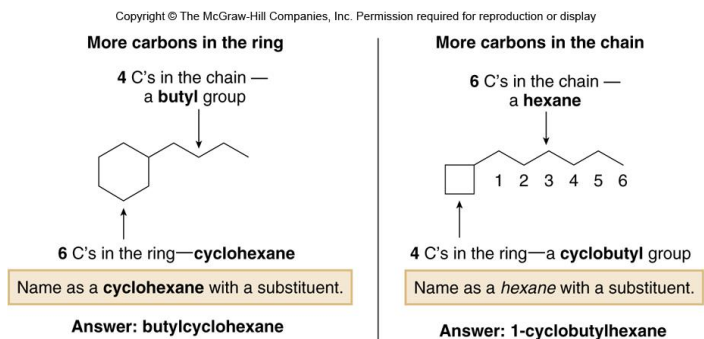
**Incorrect:** 3-ethyl-1-methylcyclohexane

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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

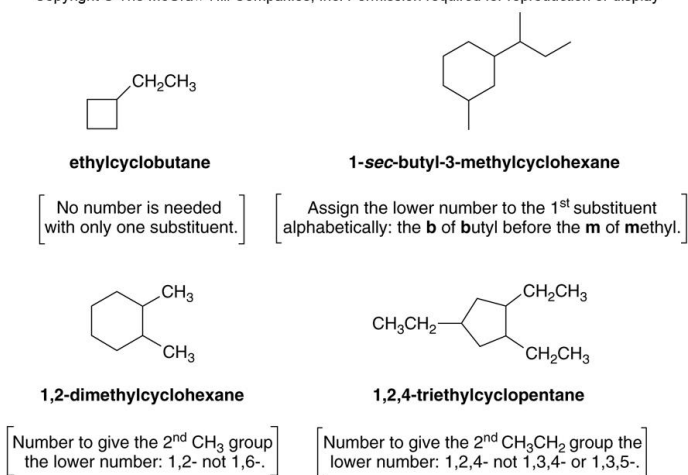


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## Examples of Naming Cycloalkanes

Figure 4.3

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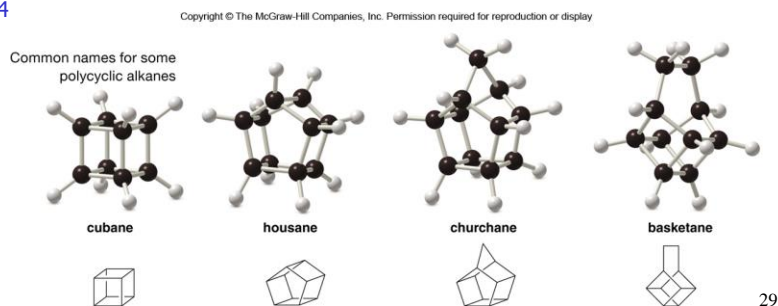


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## Common Names of Polycyclic Molecules

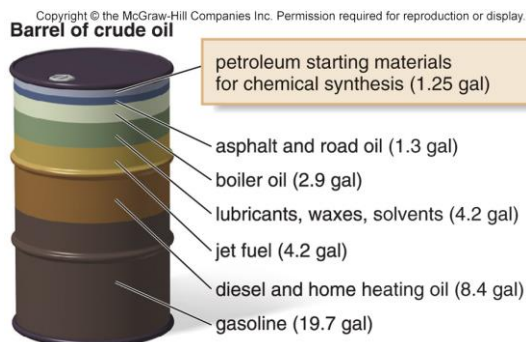
- Some organic compounds are identified using common names that **do not follow the IUPAC** system of nomenclature.
- Many of these names were given long ago before the IUPAC system was adopted, and are still widely used.
- Additionally, some names are **descriptive of shape** and structure, like those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

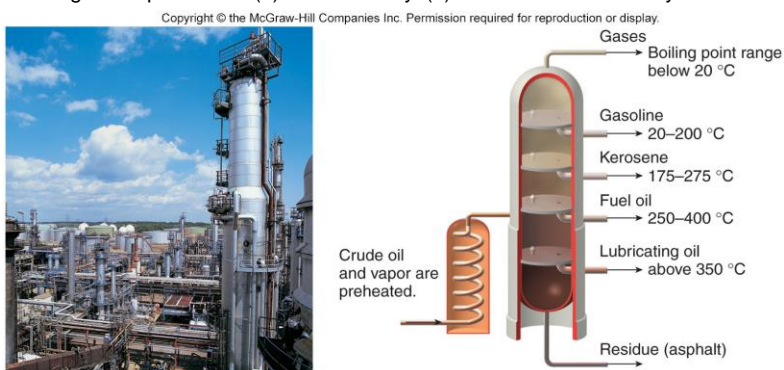
gasoline:  $C_5H_{12}$ — $C_{12}H_{26}$

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	<ul style="list-style-type: none"> <li>Alkanes have low bp's and mp's compared to more polar compounds of comparable size.</li> </ul> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{CH}_3</math> VDW bp = <math>-42^\circ\text{C}</math> mp = <math>-190^\circ\text{C}</math> </div> <div style="text-align: center;"> <math>\text{CH}_3\text{CHO}</math> VDW, DD bp = <math>21^\circ\text{C}</math> mp = <math>-121^\circ\text{C}</math> </div> </div> <p style="text-align: center;"> <b>Increasing strength of intermolecular forces</b>  <b>Increasing boiling point and melting point</b> </p>
	<ul style="list-style-type: none"> <li>Bp and mp increase as the number of carbons increases because of increased surface area.</li> </ul> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3</math> bp = <math>0^\circ\text{C}</math> mp = <math>-138^\circ\text{C}</math> </div> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3</math> bp = <math>69^\circ\text{C}</math> mp = <math>-95^\circ\text{C}</math> </div> </div> <p style="text-align: center;"> <b>Increasing surface area</b>  <b>Increasing boiling point and melting point</b> </p>
	<ul style="list-style-type: none"> <li>The bp of isomers decreases with branching because of decreased surface area.</li> </ul> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <math>(\text{CH}_3)_4\text{C}</math> bp = <math>10^\circ\text{C}</math> </div> <div style="text-align: center;"> <math>(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3</math> bp = <math>30^\circ\text{C}</math> </div> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3</math> bp = <math>36^\circ\text{C}</math> </div> </div> <p style="text-align: center;"> <b>Increasing surface area</b>  <b>Increasing boiling point</b> </p>
	<ul style="list-style-type: none"> <li>Mp increases with increased symmetry.</li> </ul> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <math>\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2</math> mp = <math>-160^\circ\text{C}</math> </div> <div style="text-align: center;"> <math>(\text{CH}_3)_4\text{C}</math> mp = <math>-17^\circ\text{C}</math> </div> </div> <p style="text-align: center;"> <b>Increasing symmetry</b>  <b>Increasing melting point</b> </p>
Solubility	<ul style="list-style-type: none"> <li>Alkanes are soluble in organic solvents.</li> <li>Alkanes are insoluble in water.</li> </ul>

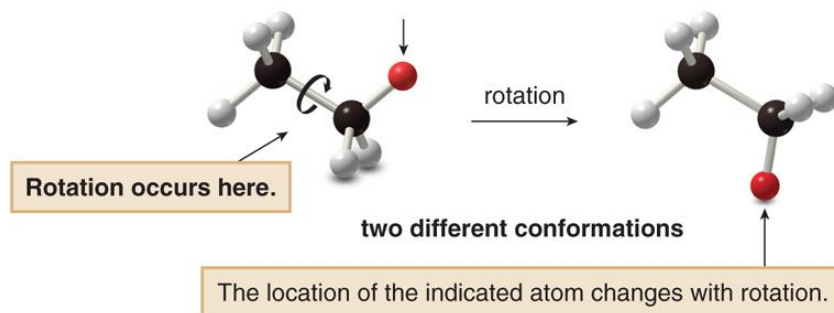
Key: bp = boiling point; mp = melting point; VDW = van der Waals; DD = dipole-dipole; HB = hydrogen bonding

33

## Conformations of Acyclic Alkanes

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

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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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eclipsed conformation

The C-H bonds are all **aligned**.

rotate 60°



staggered conformation

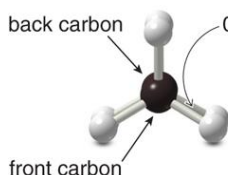
The C-H bonds in front <sup>35</sup>  
**bisect** the H-C-H bond angles in back.

## 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°.

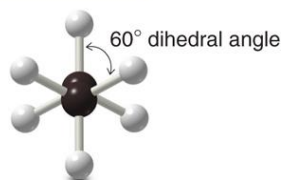
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End-on view: looking directly down the C-C bond



eclipsed conformation

rotate 60°



staggered conformation

36

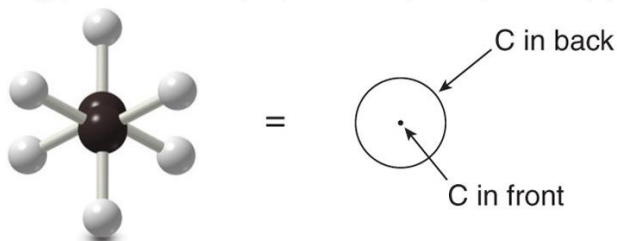
# Newman Projections

- 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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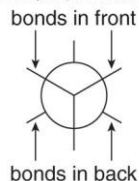
37

## Completing a Newman Projection

**Step 2.** Draw in the bonds.

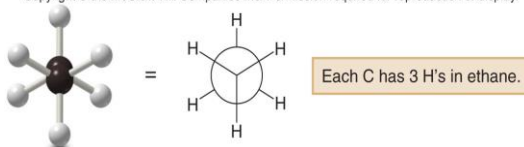
- Draw the bonds on the front C as three lines meeting at the center of the circle.
- Draw the bonds on the back C as three lines coming out of the edge of the circle.

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**Step 3.** Add the atoms on each bond.

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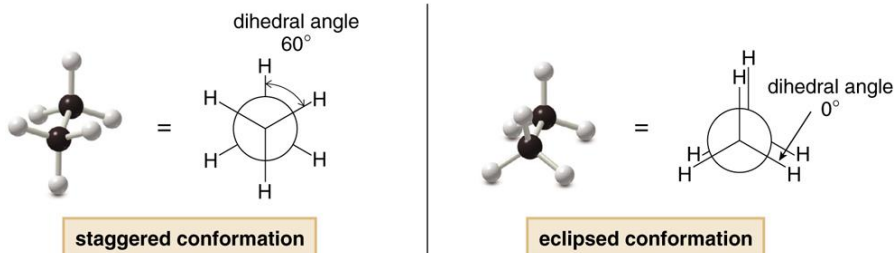


38

# Newman Projections - Ethane

Figure 4.6

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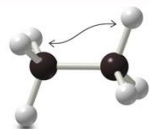
39

## 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.

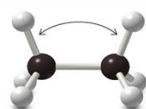
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These C-H bonds are farther apart.



staggered conformation  
side view  
more stable

These C-H bonds are closer together.



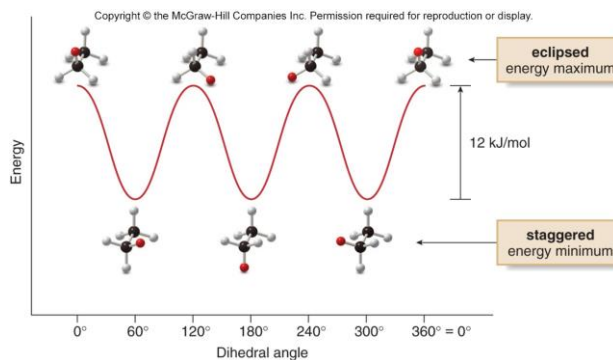
eclipsed conformation  
side view  
less stable

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.

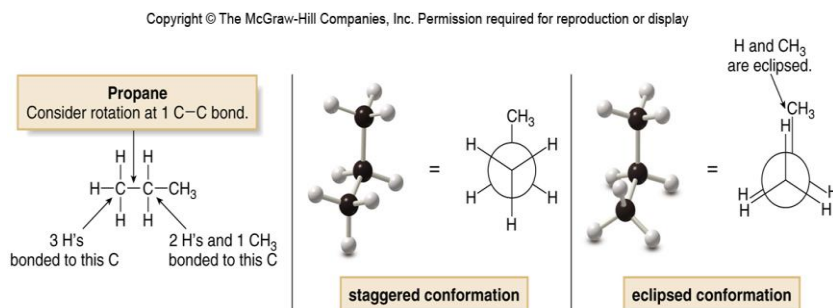
Figure 4.8



41

## Newman Projections - Propane

Figure 4.7

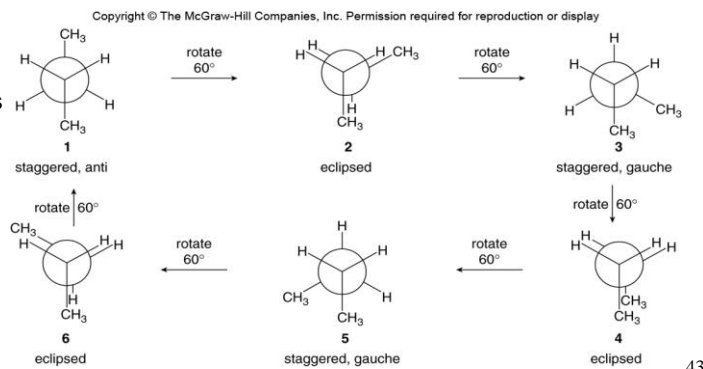


42

## Newman Projections - Butane

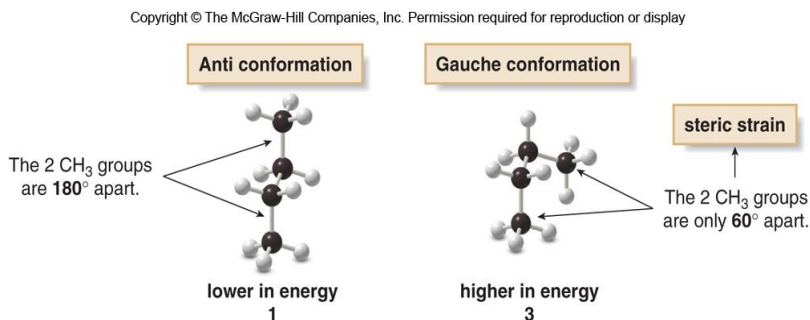
- An energy minimum and maximum occur every  $60^\circ$  as the conformation changes from staggered to eclipsed.
- Conformations that are neither staggered nor eclipsed are intermediate in energy.
- Butane and higher molecular weight alkanes have several C-C bonds, all capable of rotation.

Figure 4.9  
Six different conformations of butane



## Anti and Gauche Conformations

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

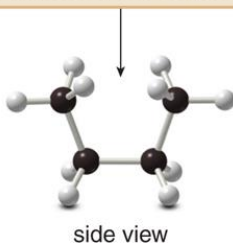


# Steric Strain

- 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 CH<sub>3</sub> groups

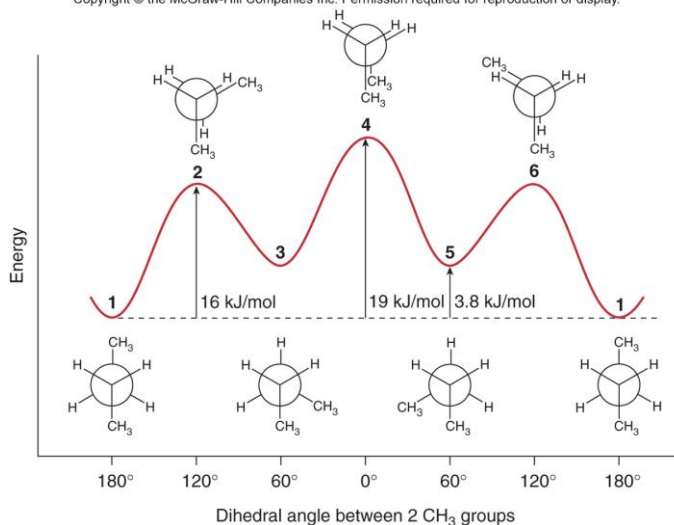


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## Conformation and Energy of Butane

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Figure 4.10



46

# 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 <sub>3</sub> eclipsing	6.0	1.4
CH <sub>3</sub> ,CH <sub>3</sub> eclipsing	11	2.6
gauche CH <sub>3</sub> groups	3.8	0.9

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

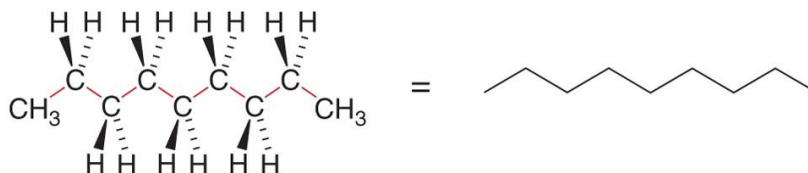
47

## 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**.



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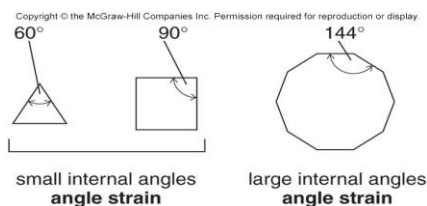


## Angle Strain in Cycloalkanes

- 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  $109.5^\circ$ .
- Cycloalkanes with more than three C atoms in the ring are not flat molecules. They are puckered to reduce strain.

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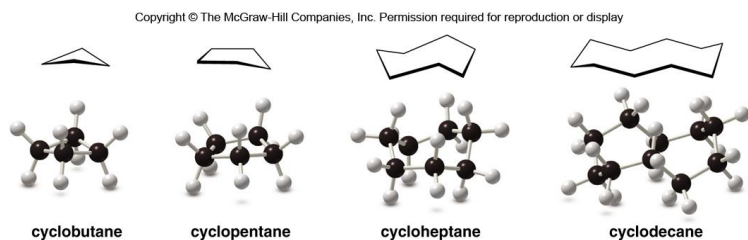
## Three to Ten Carbon Cycloalkanes



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**Cycloalkanes distort their shapes to alleviate angle and torsional strain.**

Figure 4.11

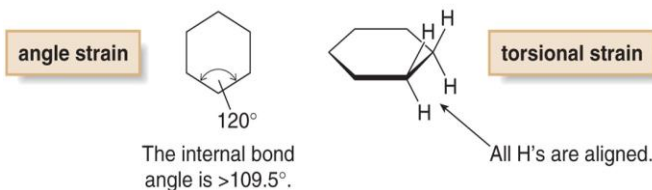


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# Cyclohexane

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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



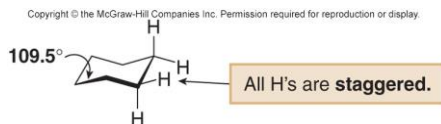
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## Chair Conformation

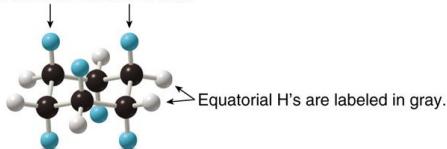
- The chair conformation is so stable because it eliminates angle strain (all C-C-C angles are 109.5°), and torsional strain (all hydrogens on adjacent C atoms are staggered).



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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.

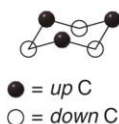
52

# Axial and Equatorial Positions

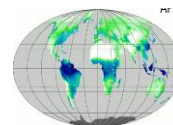
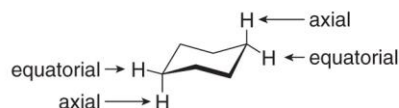
- Each C in cyclohexane has two different kinds of hydrogens:
  - (1) **Axial** hydrogens are located above and below the ring (along a perpendicular axis).
  - (2) **Equatorial** hydrogens are located in the plane of the ring (around the equator).

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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**.

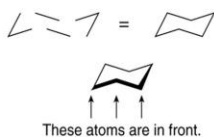
53

# Drawing Cyclohexanes

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## HOW TO Draw the Chair Form of Cyclohexane

**Step [1]** Draw the carbon skeleton.

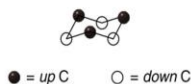


- Draw three parts of the chair: a **wedge**, a **set of parallel lines**, and **another wedge**.
- Then, join them together.
- The bottom 3 C's come out of the page, and for this reason, bonds to them are often highlighted in bold.

HOW TO, continued . . .

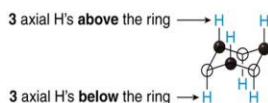
—Continued

**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.



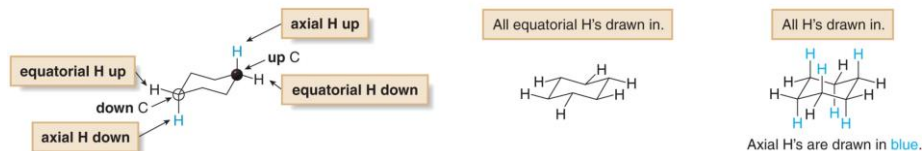
- On an *up* C the axial H is *up*.
- On a *down* C the axial H is *down*.

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# Drawing Hydrogens on Cyclohexanes

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**Step [4]** Draw in the equatorial H atoms.

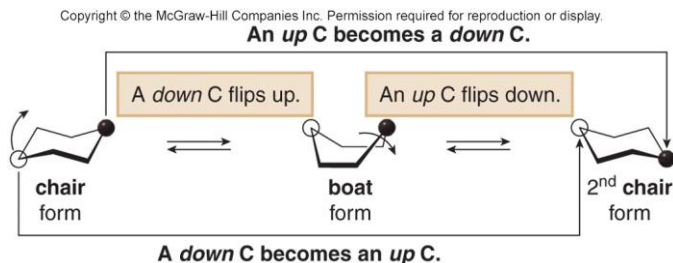
- The axial H is **down** on a down C, so the equatorial H must be up.
- The axial H is **up** on an up C, so the equatorial H must be down.



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## 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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## 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

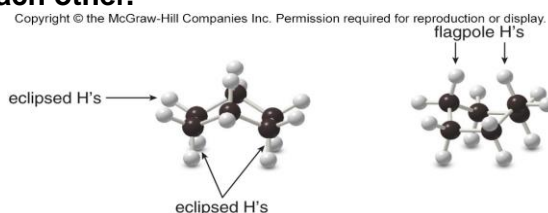


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## Boat Conformation of Cyclohexane

- 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.

Figure 4.14



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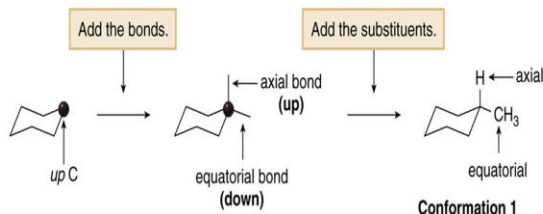
# Drawing Substituted Cyclohexanes

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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 CH<sub>3</sub>, arbitrarily placing one axial and one equatorial. In this example, the CH<sub>3</sub> group is drawn equatorial.
- This forms one of the two possible chair conformations, labeled Conformation 1.

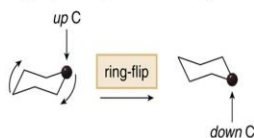


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## HOW TO Draw the Two Conformations for a Substituted Cyclohexane

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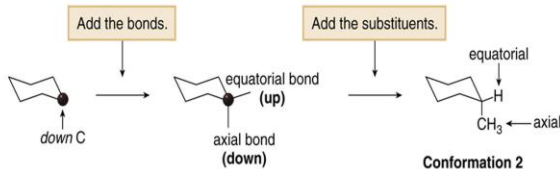
### Step [2] Ring-flip the cyclohexane ring.



- 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.

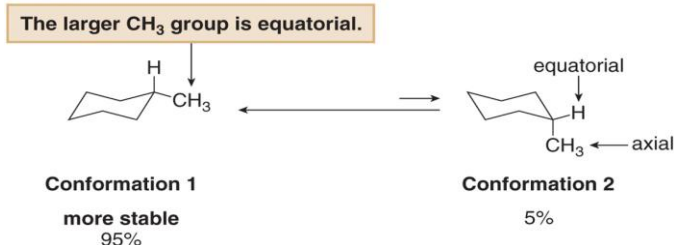


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## Chair Conformations and Energy

- 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,CH<sub>3</sub> 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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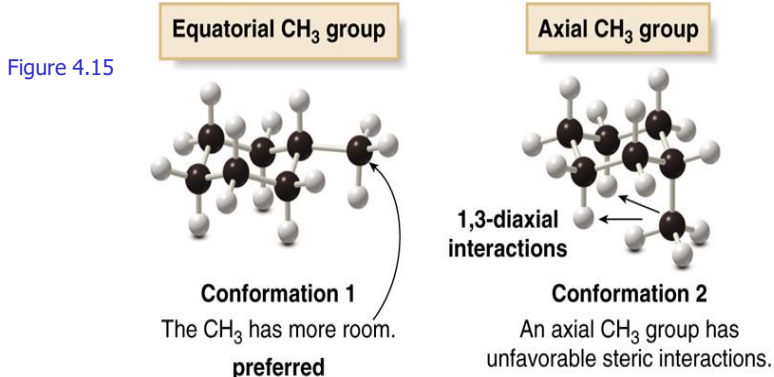


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## Preference of Equatorial Position in Substituted Cyclohexanes

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

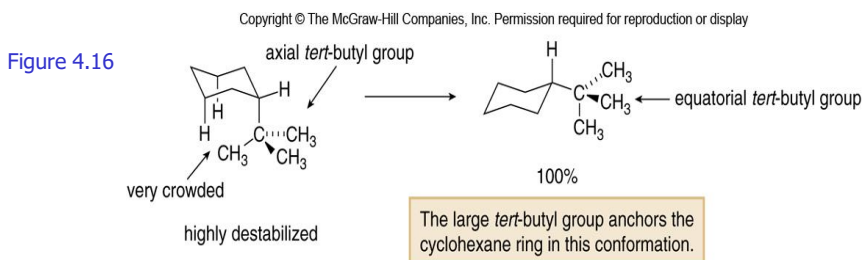
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## Preference of Equatorial Position in Substituted Cyclohexanes

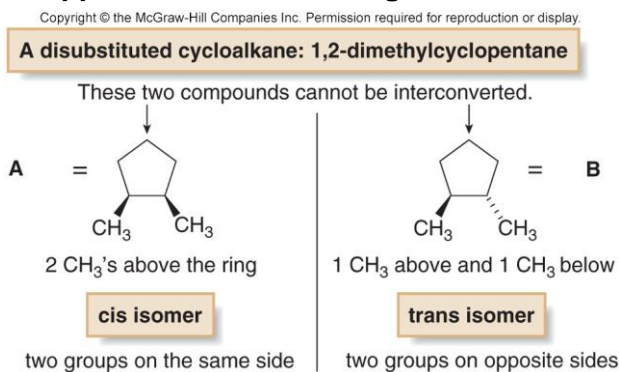
- The larger the substituent on the six-membered ring, the higher the percentage of the equatorial conformation at equilibrium.
- With a very large substituent like *tert*-butyl  $[(\text{CH}_3)_3\text{C}-]$ , essentially none of the conformation containing an axial *tert*-butyl group is present at room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



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## Disubstituted Cycloalkanes

- There are two different 1,2-dimethylcyclopentanes—one having two  $\text{CH}_3$  groups on the same side of the ring and one having them on opposite sides of the ring.



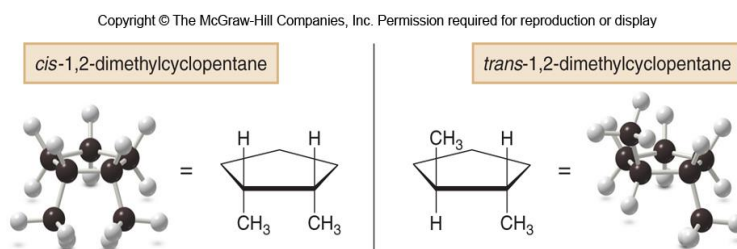
- **A and B are stereoisomers.**

64



## Cis and Trans Stereoisomers

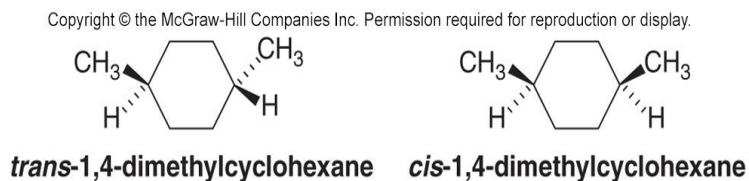
- Stereoisomers are isomers that differ only in the way the atoms are oriented in space.
- The prefixes **cis** and **trans** are used to distinguish these isomers.
- The **cis** isomer has two groups on the same side of the ring.
- The **trans** isomer has two groups on opposite sides of the ring.



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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.



66

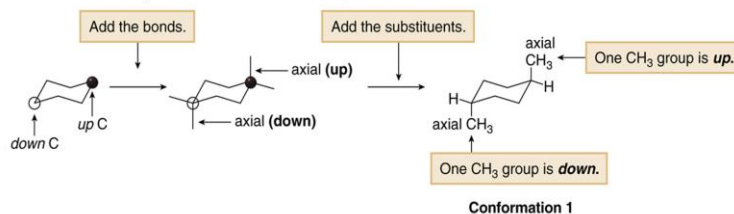
# Drawing Disubstituted Cyclohexanes

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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 CH<sub>3</sub> groups. This arrangement is said to be **diaxial**.
- This forms one of the two possible chair conformations, labeled Conformation 1.

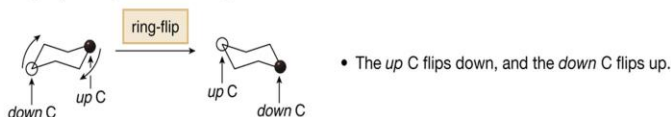


67

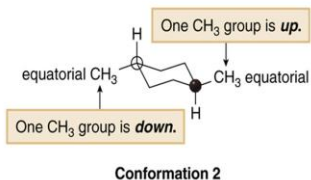
## Drawing the Second Conformation of Cyclohexanes

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### Step [2] Ring-flip the cyclohexane ring.



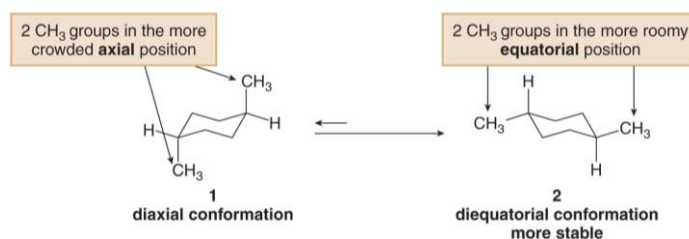
### Step [3] Add the substituents to the second conformation.



- Ring-flipping converts axial bonds to equatorial bonds, and vice versa. The diaxial CH<sub>3</sub> groups become diequatorial. This *trans* conformation is less obvious to visualize. It is still *trans*, because one CH<sub>3</sub> group is above the ring (on an *up* bond), and one is below (on a *down* bond).

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## Trans Disubstituted Cycloalkanes



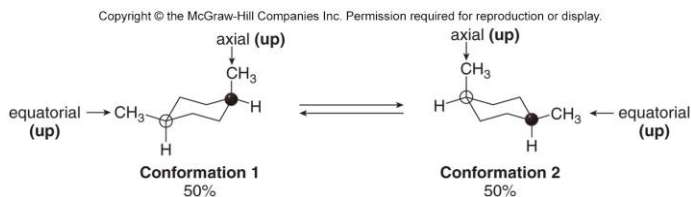
- Conformations 1 and 2 are not equally stable.
- Because conformation 2 has both CH<sub>3</sub> groups in the roomier equatorial position, it is lower in energy.
- A trans isomer has two substituents on opposite sides, one up and one down.

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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<sub>3</sub> groups drawn *up*.
- Both conformations have one CH<sub>3</sub> group axial and one equatorial, making them equally stable.

Figure 4.17



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## Cellulose vs Starch

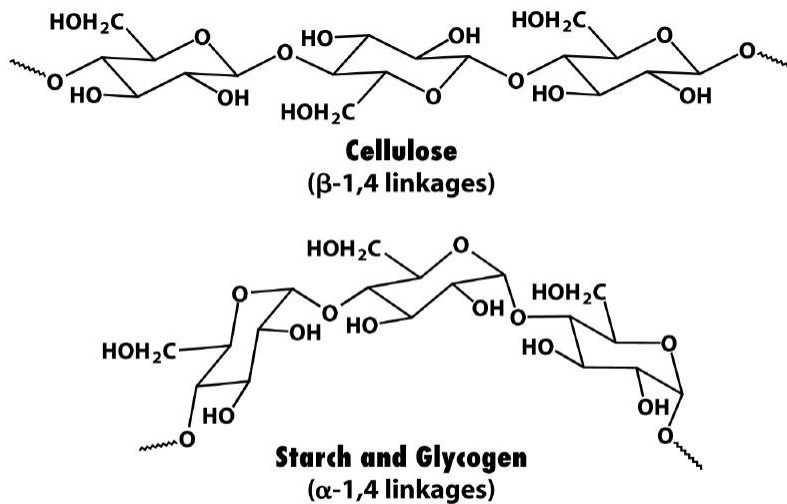


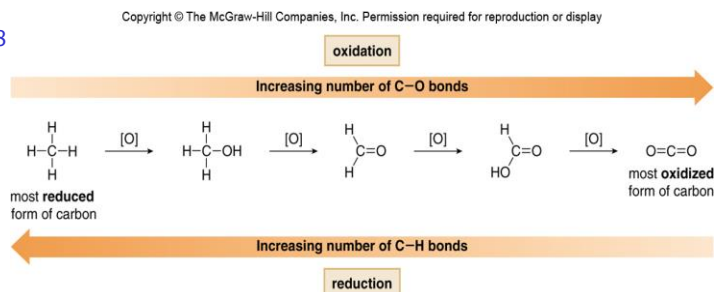
Figure 11-14  
Biochemistry, Sixth Edition  
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## Oxidation and Reduction Reactions

- 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

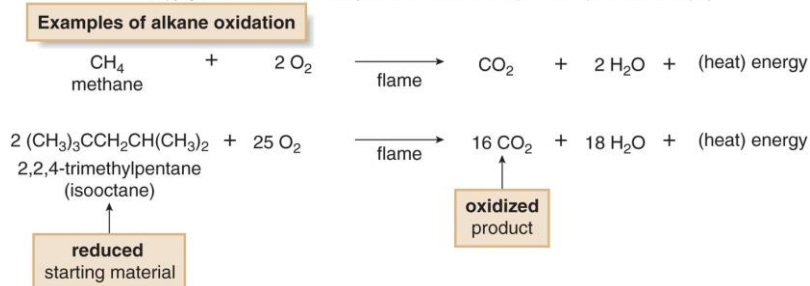


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# Combustion of Alkanes

- 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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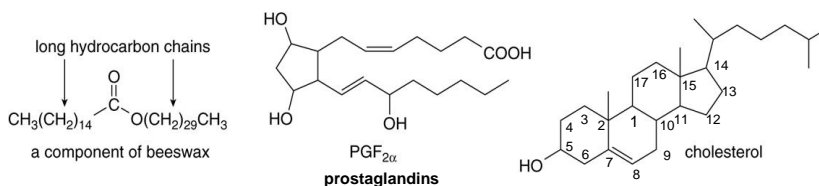
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# Lipids

- 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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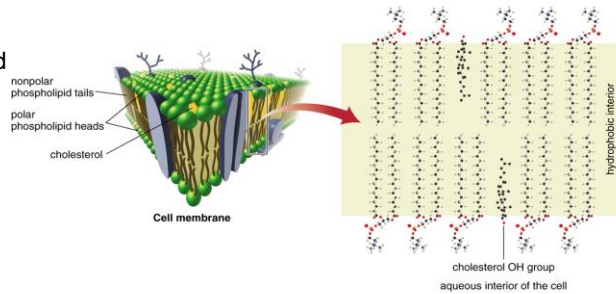
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# Cholesterol

- 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.

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aqueous exterior of the cell

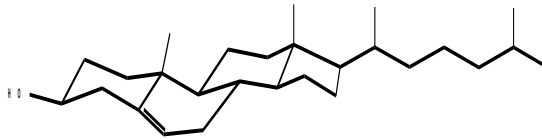
Figure 4.21  
Cholesterol embedded  
in a lipid bilayer of  
a cell membrane



- The nonpolar hydrocarbon skeleton of cholesterol is embedded in the nonpolar interior of the cell membrane. Its rigid carbon skeleton stiffens the fluid lipid bilayer, giving it strength.
- Cholesterol's polar OH group is oriented toward the aqueous media inside and outside the cell.

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# Cholesterol



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