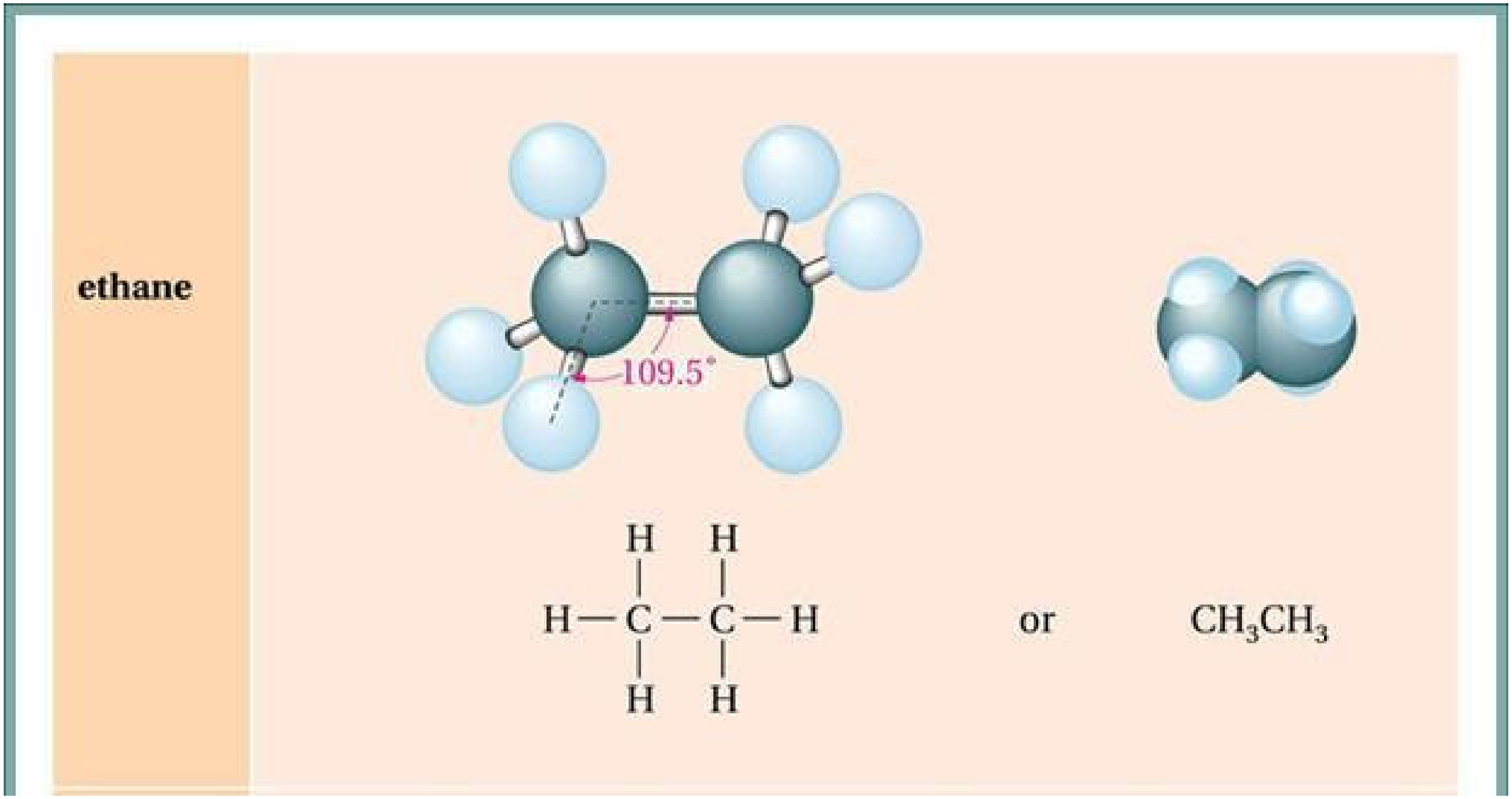
Chapter 2
Alkanes and Cycloalkanes;

Conformational and Geometric Isomerism

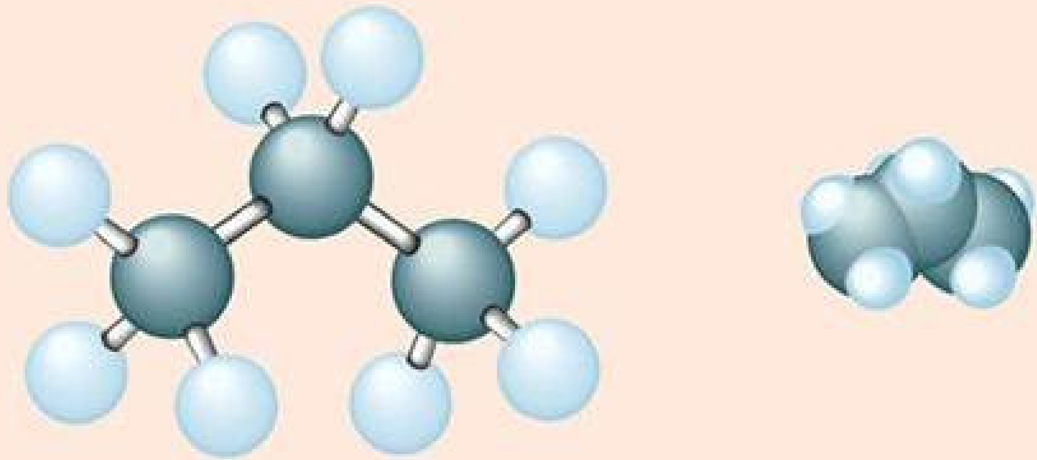
Hydrocarbons

- The main components of petroleum and natural gas.
- Hydrocarbons: compounds that contain only carbon and hydrogen
- Three main classes
  - Saturated (alkanes & cycloalkanes)
  - Unsaturated (alkenes & alkynes)
  - Aromatic (benzene)

2.1 The Structure of Alkanes



propane



$$\begin{array}{ccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array} \quad \text{or} \quad CH_3CH_2CH_3$$

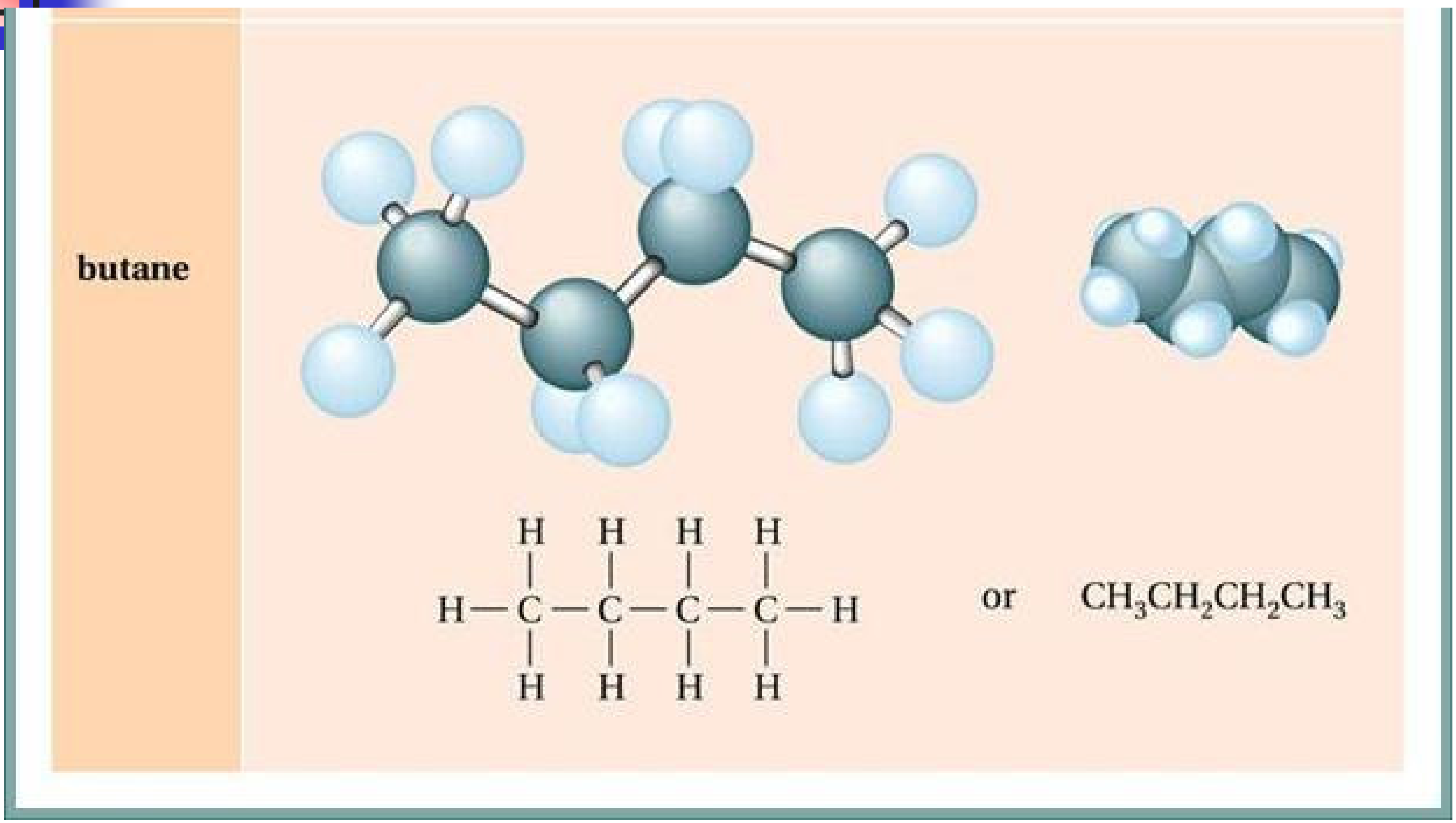

butane
or
$CH_3CH_2CH_2CH_3$

Table 2.1 Names and formulas of the first ten unbranched alkanes

Table 2.1 **Names and formulas of the first ten unbranched alkanes**

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

- The number of structural isomers possible for a given molecular formula increases rapidly with

Molecular Formula	Possible Number of Constitutional Isomers
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{30}H_{62}$	4,111,846,763
$C_{40}H_{82}$	62,481,801,147,341

- Constitutional isomers have different physical properties (melting point, boiling point, densities etc.)
  - Constitutional isomers have the same molecular formula but different connectivity of atoms

Molecular Formula	Structural Formula	mp (°C)	bp (°C)[a] (1 atm)	Density[b] (g mL^{-1})	Index of Refraction[c] (n_D 20°C)
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	−95	68.7	0.6594^{20}	1.3748
C_6H_{14}	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_2CH_3$	−153.7	60.3	0.6532^{20}	1.3714
C_6H_{14}	$CH_3CH_2\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	−118	63.3	0.6643^{20}	1.3765
C_6H_{14}	$CH_3\underset{\underset{CH_3}{\vert}}{C}H-\underset{\underset{CH_3}{\vert}}{C}HCH_3$	−128.8	58	0.6616^{20}	1.3750
C_6H_{14}	$CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2CH_3$	−98	49.7	0.6492^{20}	1.3688

[a] Unless otherwise indicated, all boiling points given in this book are at 1 atm or 760 torr.
[b] The superscript indicates the temperature at which the density was measured.
[c] The index of refraction is a measure of the ability of the alkane to bend (refract) light rays. The values reported are for light of the D line of the sodium spectrum (n_D).

notes

- Alkanes fit the general formula

$$C_nH_{2n+2}$$

• A cycloalkane has two fewer hydrogens than the corresponding alkane. Thus, the general formula for a cycloalkane is

$$C_nH_{2n}$$

notes

- Normal alkanes (or n-alkanes)
  - Unbranched
  - Homologous series: compounds differ by a regular unit of structure and share similar properties
  - Methylene group: $-CH_2-$

Example

- Which of t

1. C_7H_{18}
2. C_7H_{16}
3. C_8H_{16}
4. $C_{27}H_{56}$

Answer:

The formulas in parts 2 and 4 fit the general formula C_nH_{2n+2} and are alkanes. 3 has two fewer hydrogens than called for by the alkane formula and must be either an alkene or a cycloalkane.

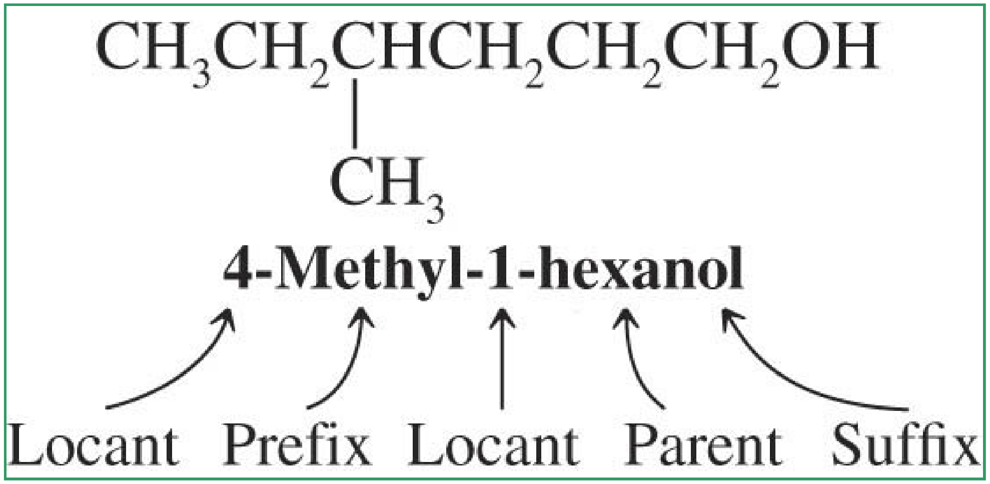
1 is an impossible molecular formula; it has too many hydrogens for the number of carbons.

2.2 Nomenclature of Organic Compounds

- Before the end of the 19th century compounds were named using nonsystematic nomenclature
- These “common” or “trivial” names were often based on the source of the compound or a physical property
- The International Union of Pure and Applied Chemistry (IUPAC) started devising a systematic approach to nomenclature in 1892
- The fundamental principle in devising the system was that each different compound should have a unique unambiguous name
- The basis for all IUPAC nomenclature is the set of rules used for naming alkanes

IUPAC Substitutive Nomenclature

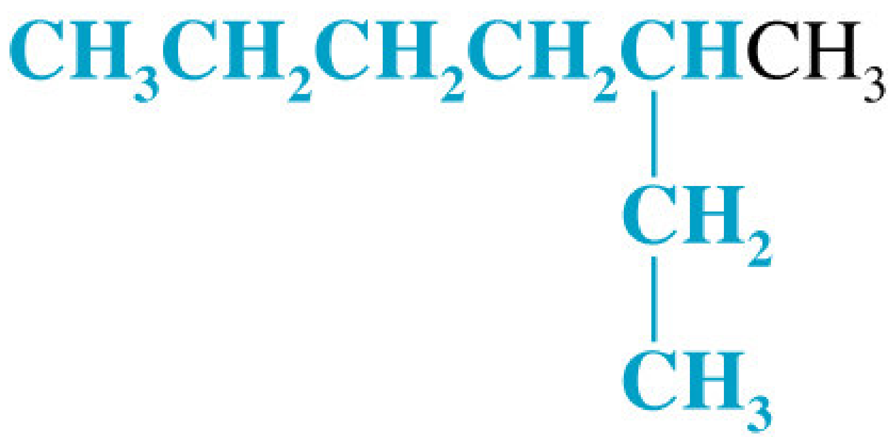
- An IUPAC name may have up to 4 features: locants, prefixes, parent compound and suffixes



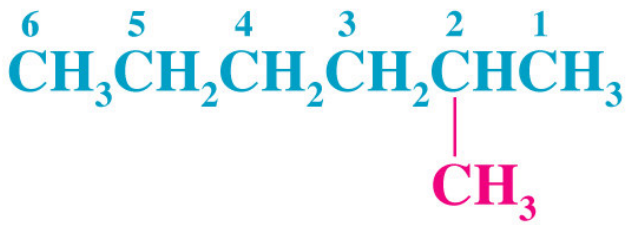
- Numbering generally starts from the end of the chain which is closest to the group named in the suffix

2.3 IUPAC Rules for Naming Alkanes

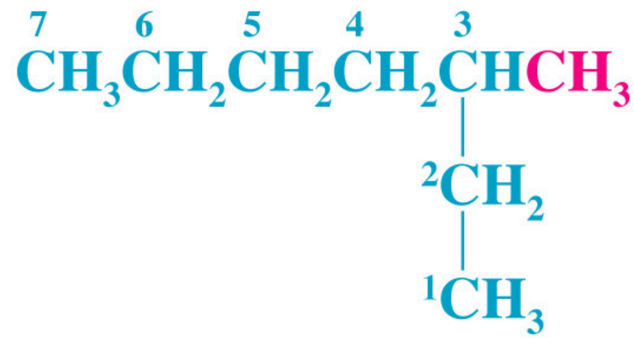
Locate the longest continuous chain of carbons; this is the parent chain and determines the parent name.



- Number the longest chain beginning with the end of the chain nearer the substituent
- Designate the location of the substituent



2-Methylhexane



3-Methylheptane

•When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain

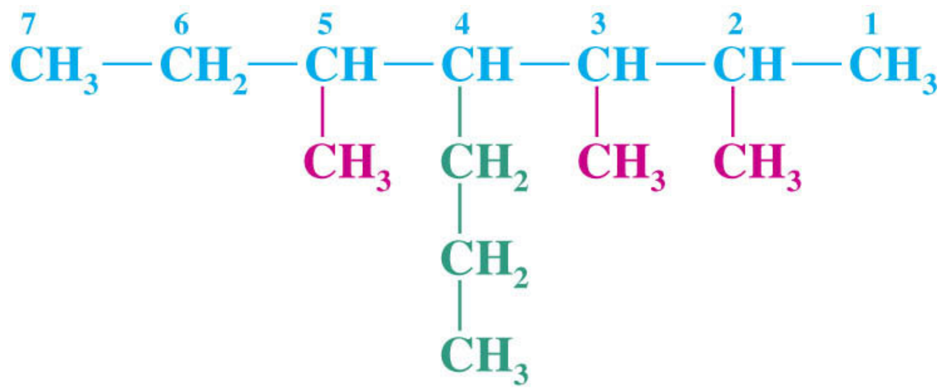
•Substituents are listed alphabetically

Nomenclature of Unbranched Alkyl groups

The unbranched alkyl groups are obtained by removing one hydrogen from the alkane and named by replacing the **-ane** of the corresponding alkane with **-yl**

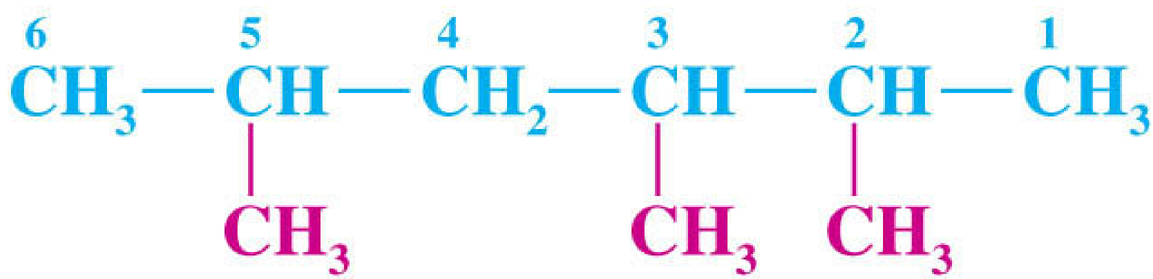
ALKANE		ALKYL GROUP	ABBREVIATION
$CH_3—H$ **Methane**	becomes	$CH_3—$ **Methyl**	Me—
$CH_3CH_2—H$ **Ethane**	becomes	$CH_3CH_2—$ **Ethyl**	Et—
$CH_3CH_2CH_2—H$ **Propane**	becomes	$CH_3CH_2CH_2—$ **Propyl**	Pr—
$CH_3CH_2CH_2CH_2—H$ **Butane**	becomes	$CH_3CH_2CH_2CH_2—$ **Butyl**	Bu—

- When two or more substituents are identical, use the prefixes *di-*, *tri-*, *tetra-* etc.
    - Commas are used to separate numbers from each other
    - The prefixes are used in alphabetical prioritization
- When two chains of equal length compete to be parent, choose the chain with the greatest number of substituents



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

•When branching first occurs at an equal distance from either end of the parent chain, choose the name that gives the lower number at the first point of difference

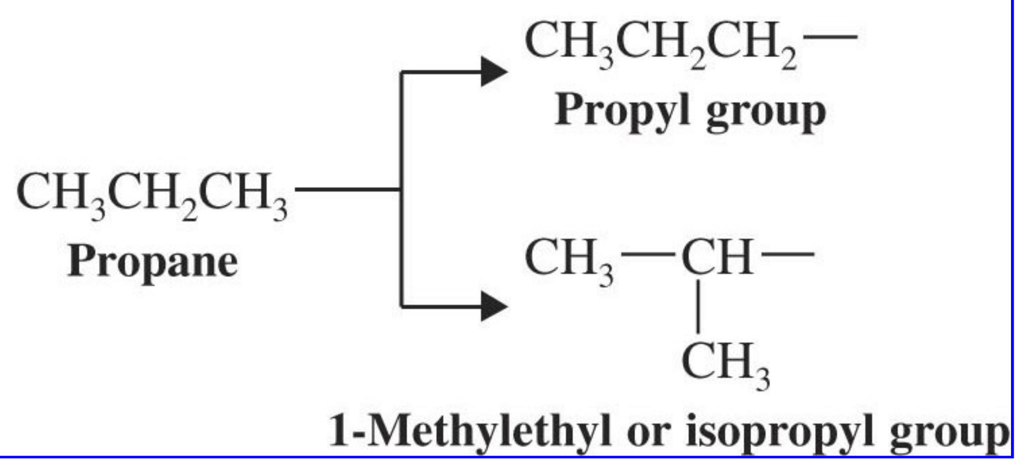


2,3,5-Trimethylhexane
(*not* 2,4,5-trimethylhexane)

Nomenclature of Branched Alkyl Chains

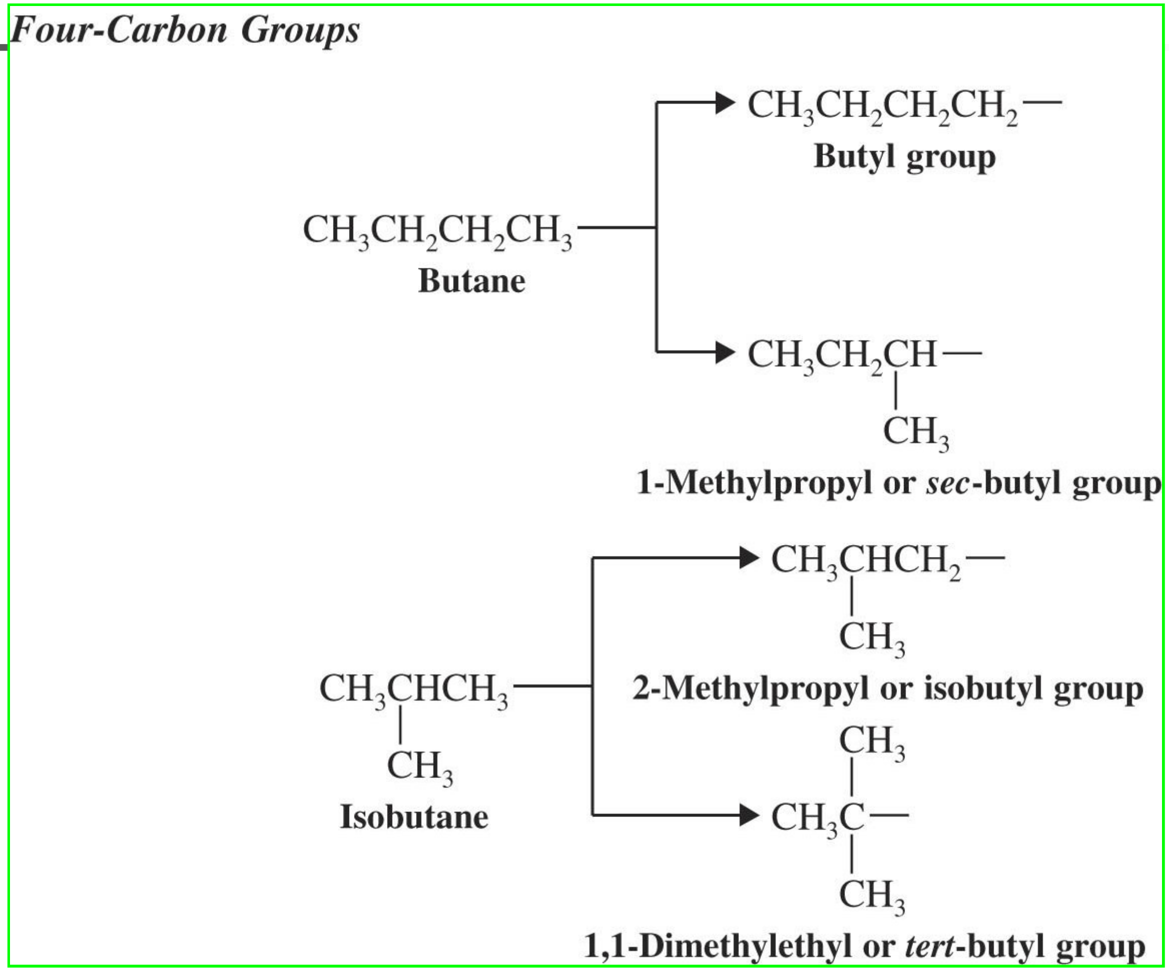
- Two alkyl groups can be derived from propane

Three-Carbon Groups

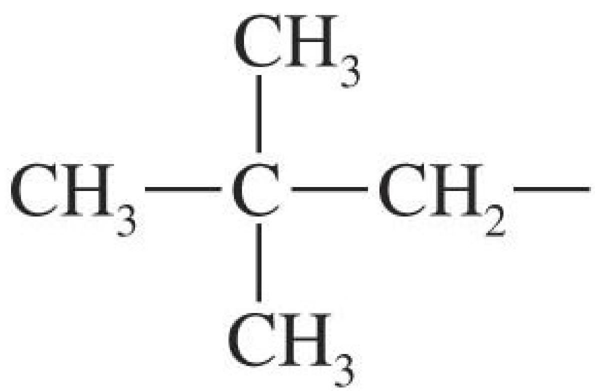


(*i*-Pr-)

- Four groups can be derived from the butane isomers



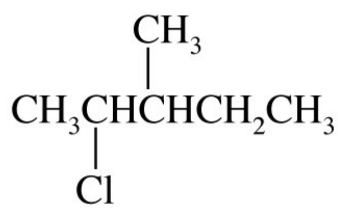
The neopentyl group is a common branched alkyl group



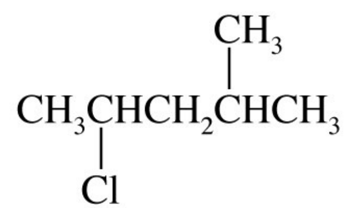
2,2-Dimethylpropyl or neopentyl group

Nomenclature of Alkyl Halides

- In IUPAC nomenclature halides are named as substituents on the parent chain
  - Halo and alkyl substituents are considered to be of equal ranking



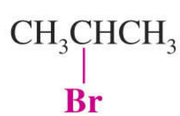
2-Chloro-3-methylpentane



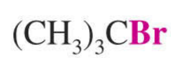
2-Chloro-4-methylpentane

- In common nomenclature the simple haloalkanes are named as alkyl halides
  - Common nomenclature of simple alkyl halides is accepted by IUPAC and still used

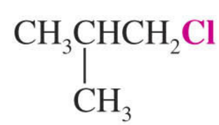
Ethyl chloride



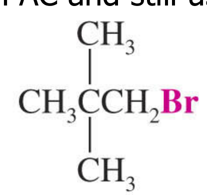
Isopropyl bromide



***tert*-Butyl bromide**



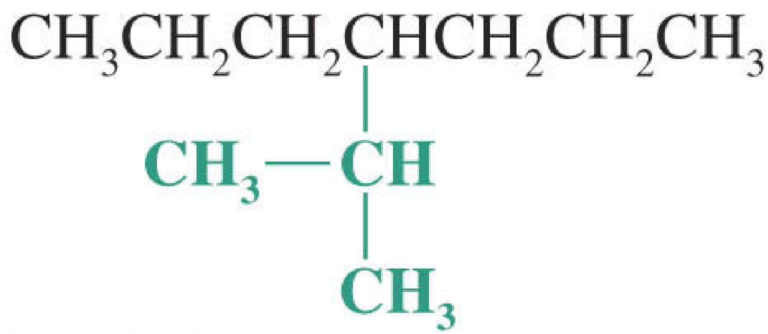
Isobutyl chloride



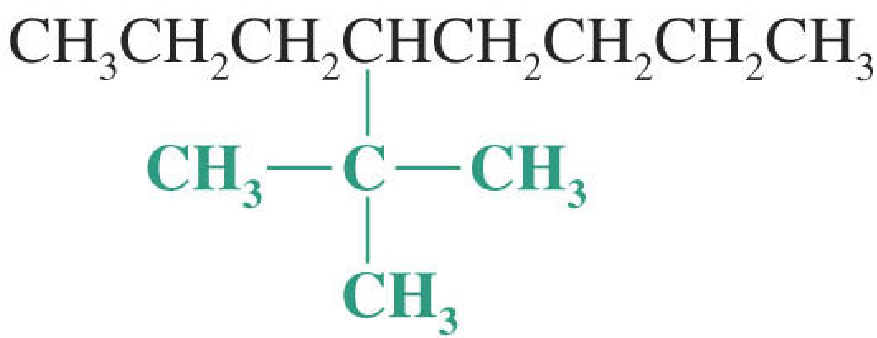
Neopentyl bromide

F-	Cl-	Br-	I-
Flouro-	Chloro-	Bromo-	Iodo-

Examples



4-(1-Methylethyl)heptane or 4-isopropylheptane

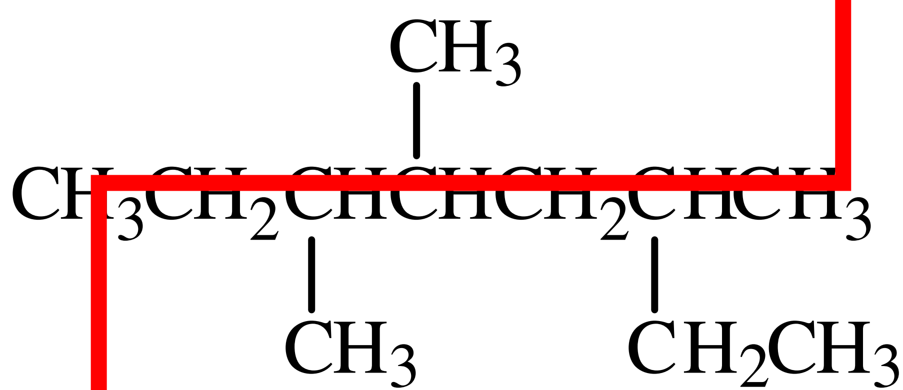


4-(1,1-Dimethylethyl)octane or 4-*tert*-butyloctane

Examples

Correct Answer

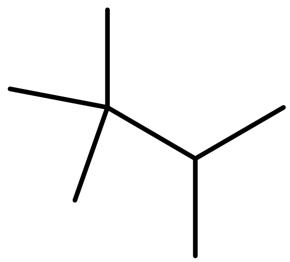
- The correct IUPAC name for the following molecule is:

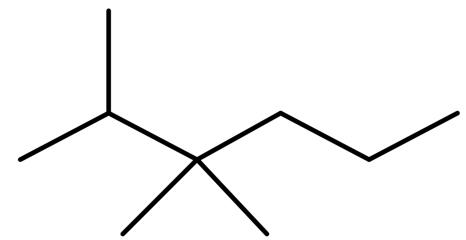


a. 6-ethyl-3,4-dimethylheptane
b. 2-ethyl-4,5-dimethylheptane
c. 3,4,6-trimethyloctane
d. 3,5,6-trimethyloctane
e. none of these

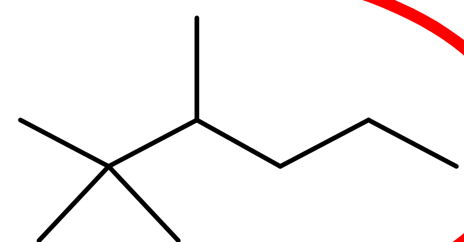
Example

- The structural formula for 2,2,3-trimethylhexane is

a. 

b. 

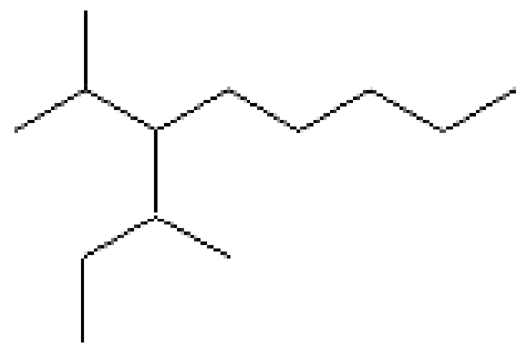
c. $(CH_3)_2CCH_2CH_3$ with CH_3 on the central C

d. 

e. $(CH_3)_3CCHCH_3$ with CH_3 on the CH

Example

What is a correct name for the following compound?



A)3-Isobutyl-2-methylheptane
B)3-sec-Butyl-2-methyloctane
C)5-Isobutyl-6-methylheptane
D)2-Ethyl-3-isopropyloctane
E)4-Isopropyl-3-methylnonane

Example

- 12.What is the common name for this compound?

A)Isobutyl bromide

B)tert-Butyl bromide

C)Butyl bromide

D)sec-Butyl bromide

E)Bromo-sec-butane

$$\begin{array}{c} \qquad CH_3 \\ \qquad | \\ CH_3CHCH_2Br \end{array}$$

example

- The correct IUPAC name for

```
                CH(CH3)2
                |
CH3CHCH2CCH3
     |          |
     Br         Cl
```

is

A)2-Bromo-4-chloro-4-isopropylpentane
B)4-Bromo-2-chloro-2-isopropylpentane
C)5-Bromo-3-chloro-2,3-dimethylhexane
D)2-Bromo-4-chloro-4,5-dimethylhexane
E)2-(2-Bromopropyl)-2-chloro-3-methylbutane

2.6 Sources of Alkanes

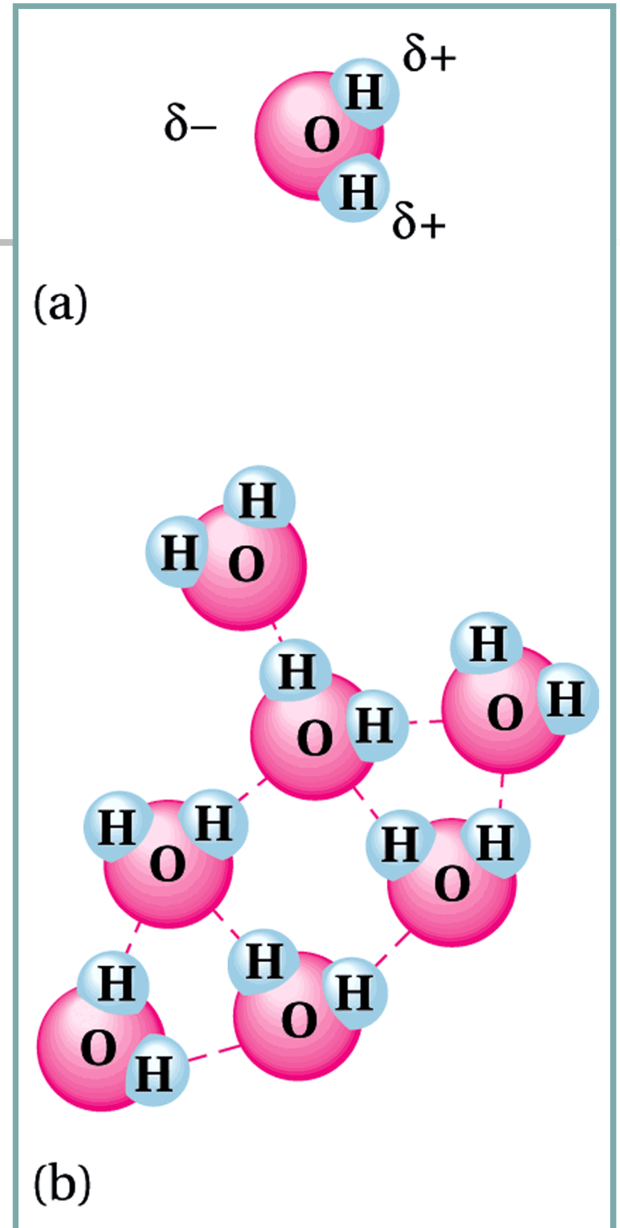
- Petroleum and natural gas are the two most important natural sources of alkanes

2.7 Physical Properties of Alkanes

Nonbonding Intermolecular Forces

- Alkanes are nonpolar and insoluble in water.
- Alkanes are nearly purely covalent.
- Protecting wax coatings on leaves and fruits.
  - Cabbage & broccoli: n-$C_{29}H_{60}$
  - Tobacco leaves: n-$C_{31}H_{64}$
  - Similar hydrocarbons are found in beeswax

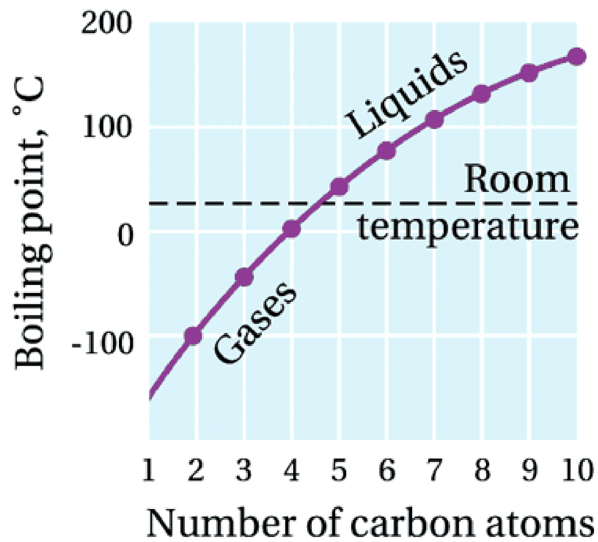
Figure 2.2
Hydrogen bonding



Physical Properties

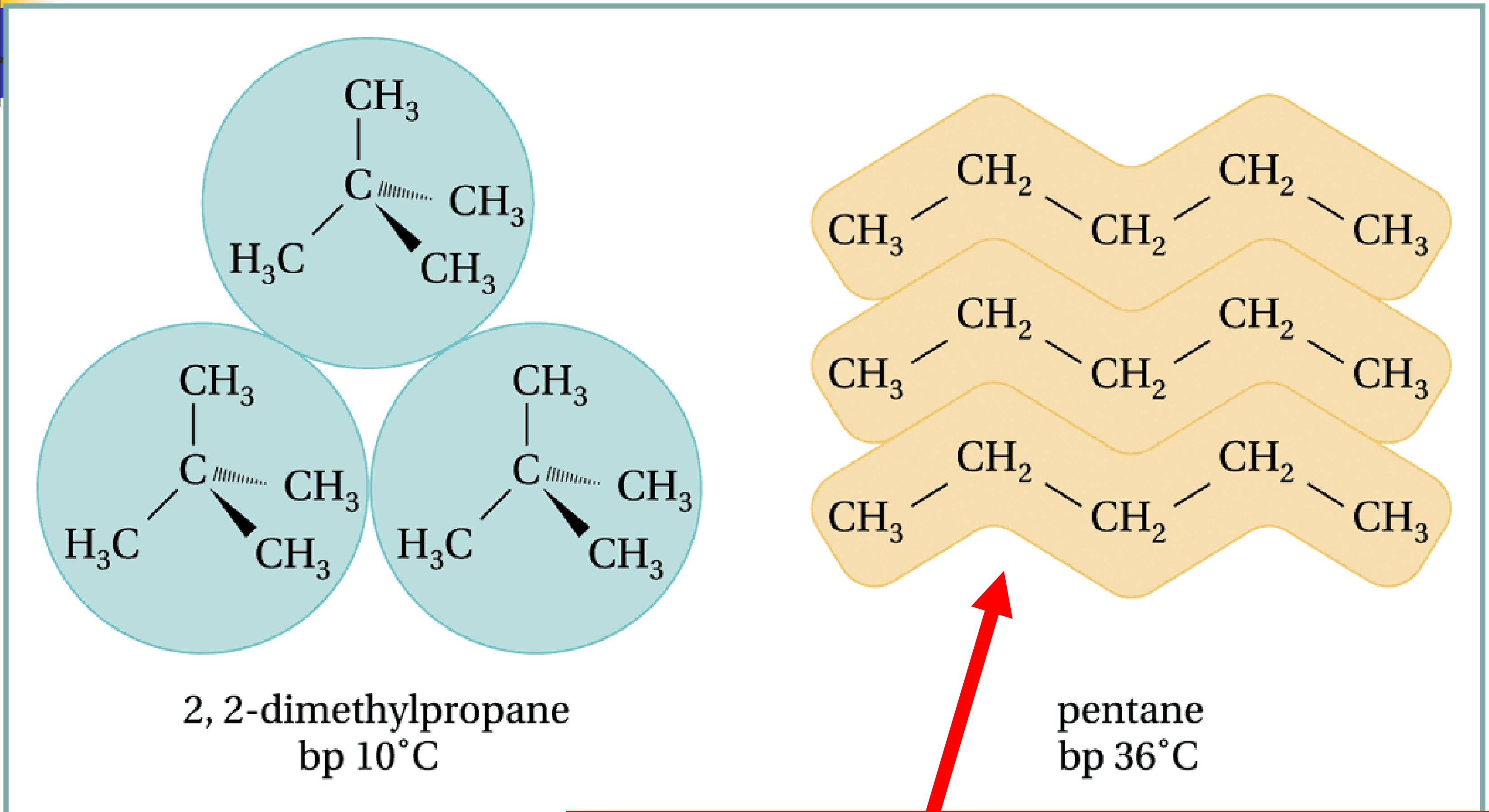
- Alkanes (nonpolar) have lower boiling points for a given molecular weight than most other organic compouns.
- van der Waals attractions.

Figure 2.3 Boiling points of normal alkanes



Name	Formula	Boiling point, ˚C
pentane	$CH_3CH_2CH_2CH_2CH_3$	36
2-methylbutane (isopentane)	$CH_3CH(CH_3)CH_2CH_3$	28
2, 2-dimethyl-propane (neopentane)	$CH_3C(CH_3)_2CH_3$	10

Figure 2.4 2-2-Dimethylpropane and pentane

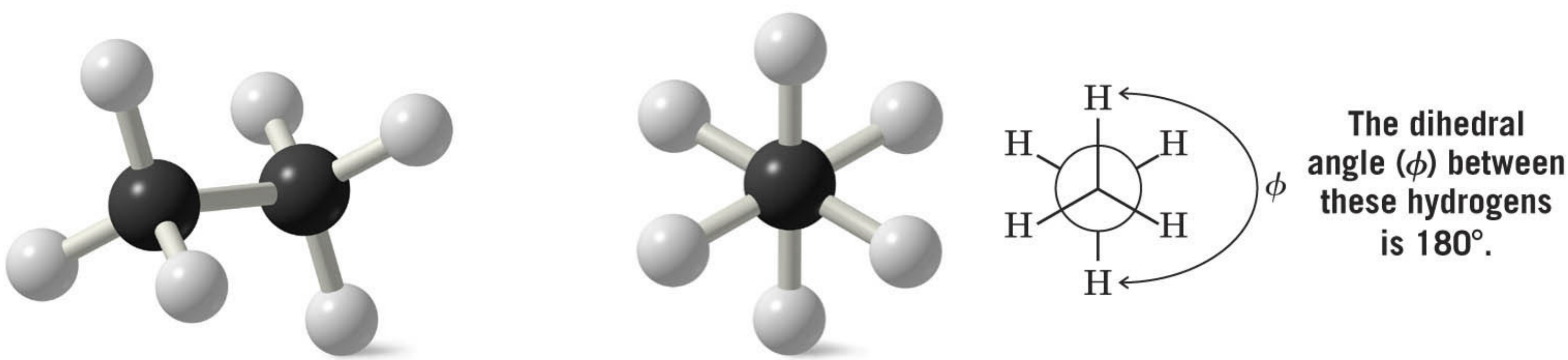


Experience more van der Waals attractions

Coformations of Alkanes

Sigma Bonds & Bond Rotation

- Ethane has relatively free rotation around the carbon-carbon bond
- The staggered conformation has C-H bonds on adjacent carbons as far apart from each other as possible
  - The drawing to the right is called a Newman projection



(a) (b)

- The eclipsed conformation has all C-H bonds on adjacent carbons directly on top of each other

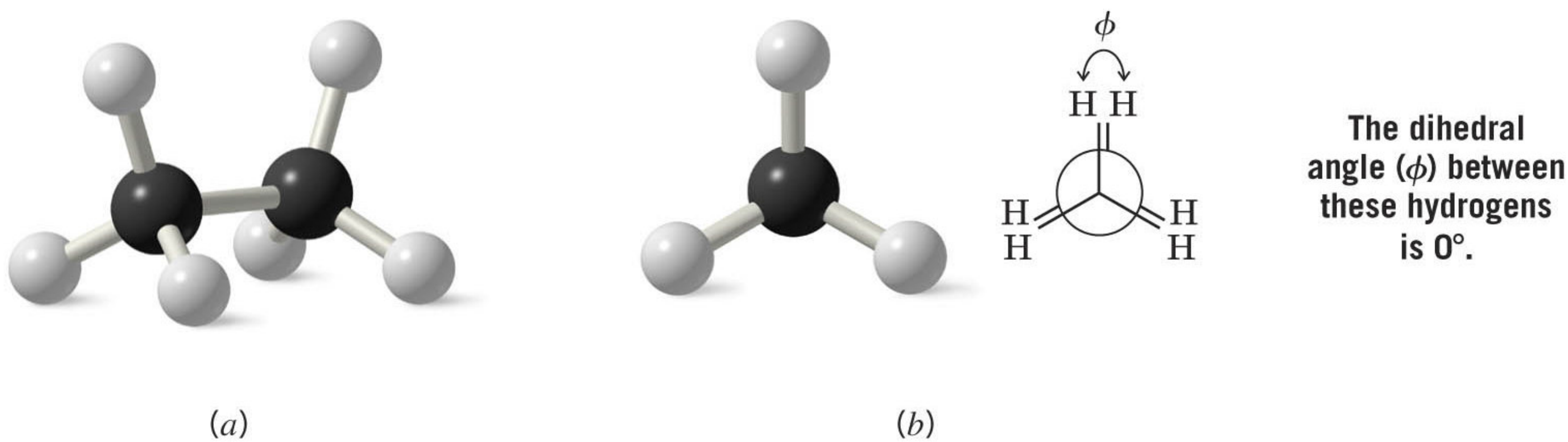
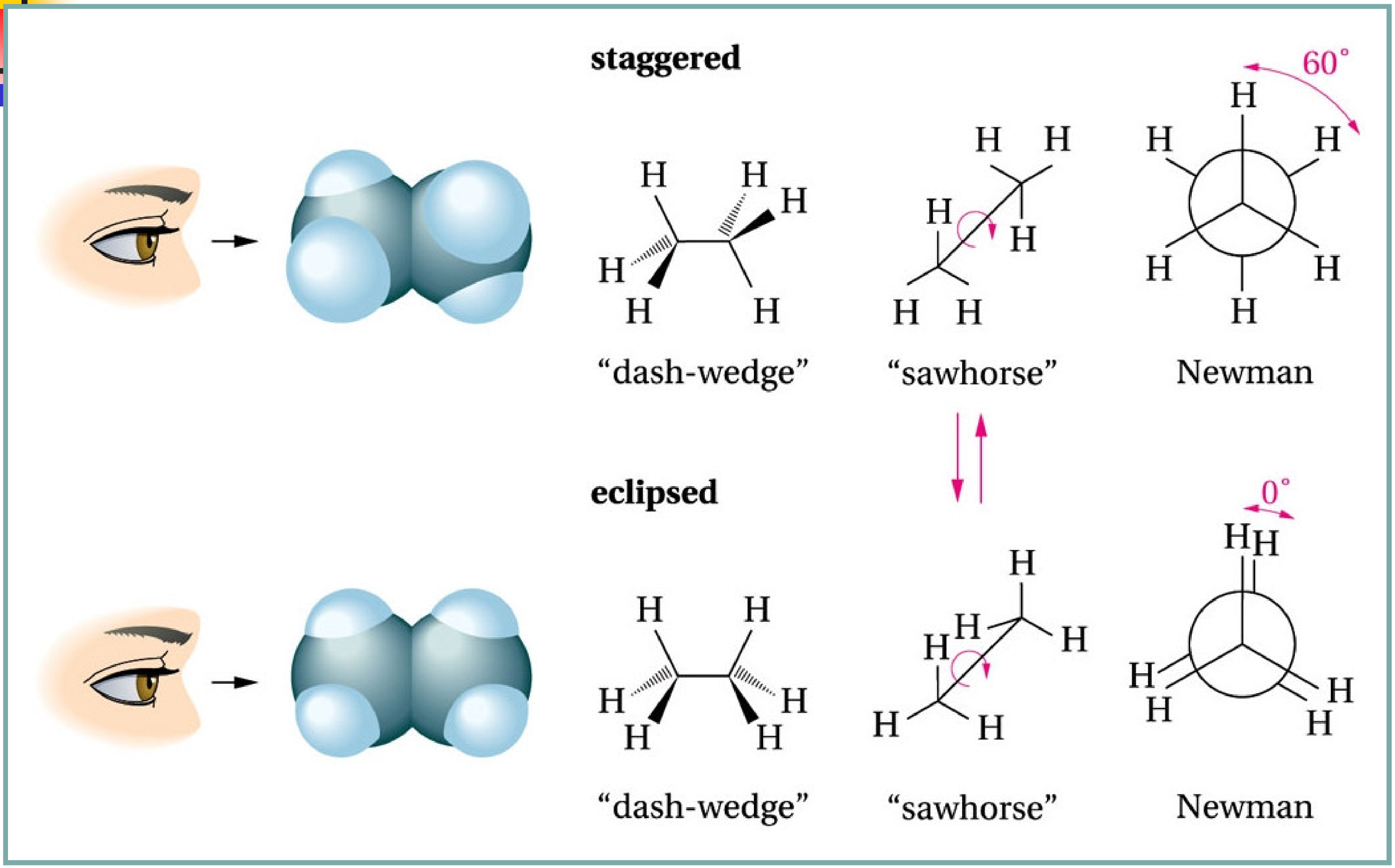
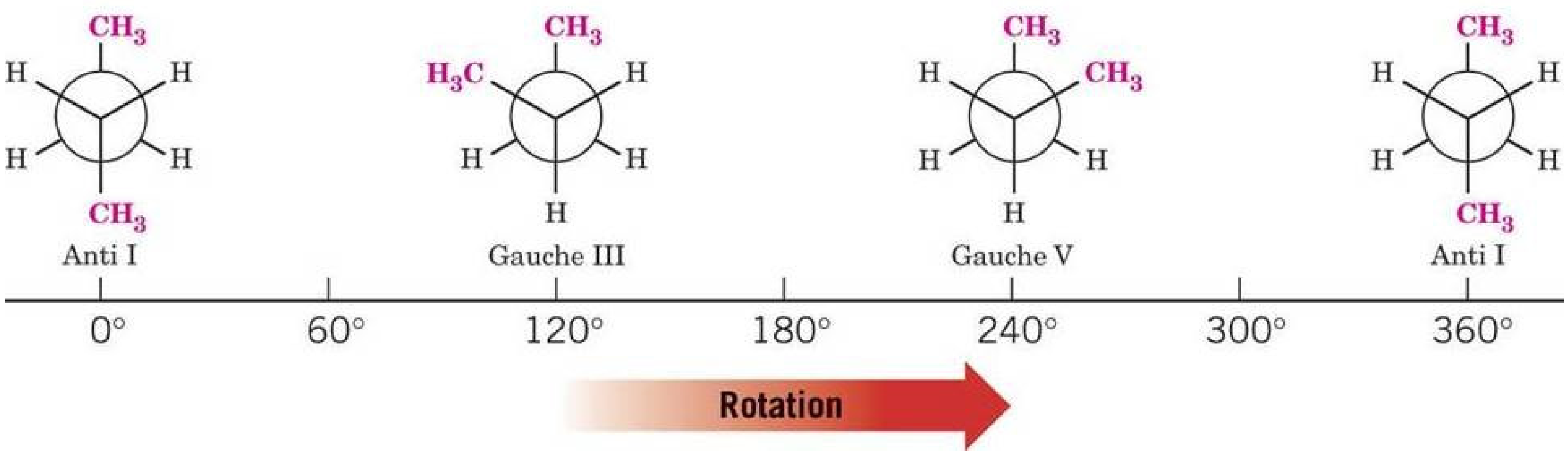


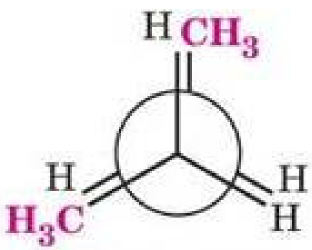
Figure 2.5 Two of the possible conformations of ethane: staggered and eclipsed



animations

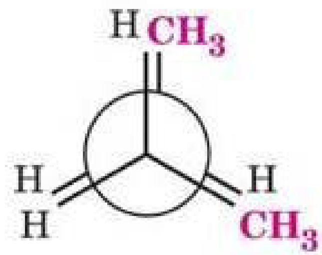
butane


CH3
H
H
H
H
CH3
Anti I
CH3
H3C
H
H
H
H
Gauche III
CH3
H
CH3
H
H
H
Gauche V
CH3
H
H
H
H
CH3
Anti I
0°
60°
120°
180°
240°
300°
360°
Rotation



Eclipsed II

Eclipsed IV



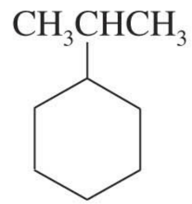
Eclipsed VI

Cycloalkane Nomenclature

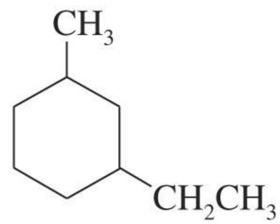
Conformation

Nomenclature of Cycloalkanes

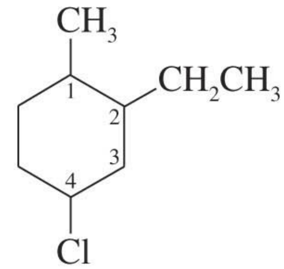
- The prefix cyclo- is added to the name of the alkane with the same number of carbons
  - When one substituent is present it is assumed to be at position one and is not numbered
  - When two alkyl substituents are present the one with alphabetical priority is given position 1
  - Numbering continues to give the other substituent the lowest number
  - Hydroxyl has higher priority than alkyl and is given position 1
  - If a long chain is attached to a ring with fewer carbons, the cycloalkane is considered the substituent



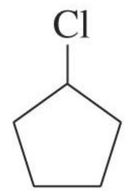
Isopropylcyclohexane



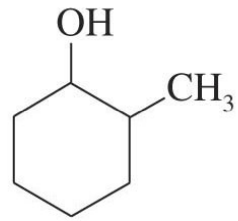
1-Ethyl-3-methylcyclohexane
(*not* 1-ethyl-5-methylcyclohexane)



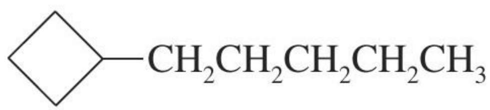
4-Chloro-2-ethyl-1-methylcyclohexane
(*not* 1-chloro-3-ethyl-4-methylcyclohexane)



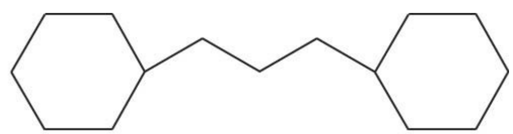
Chlorocyclopentane



2-Methylcyclohexanol



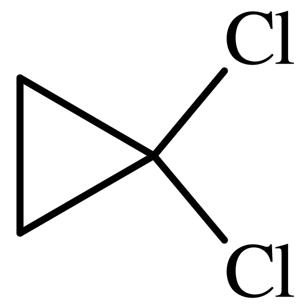
1-Cyclobutylpentane



1,3-Dicyclohexylpropane

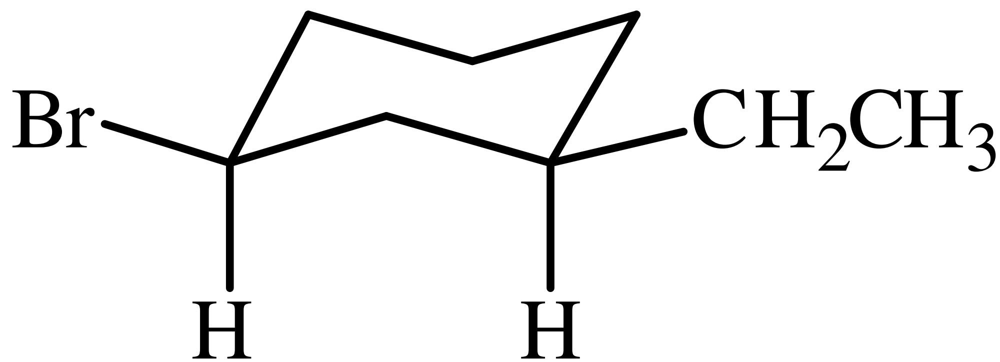
examples

- What is a correct name for the following molecule?



1,1-dichlorocyclopropane

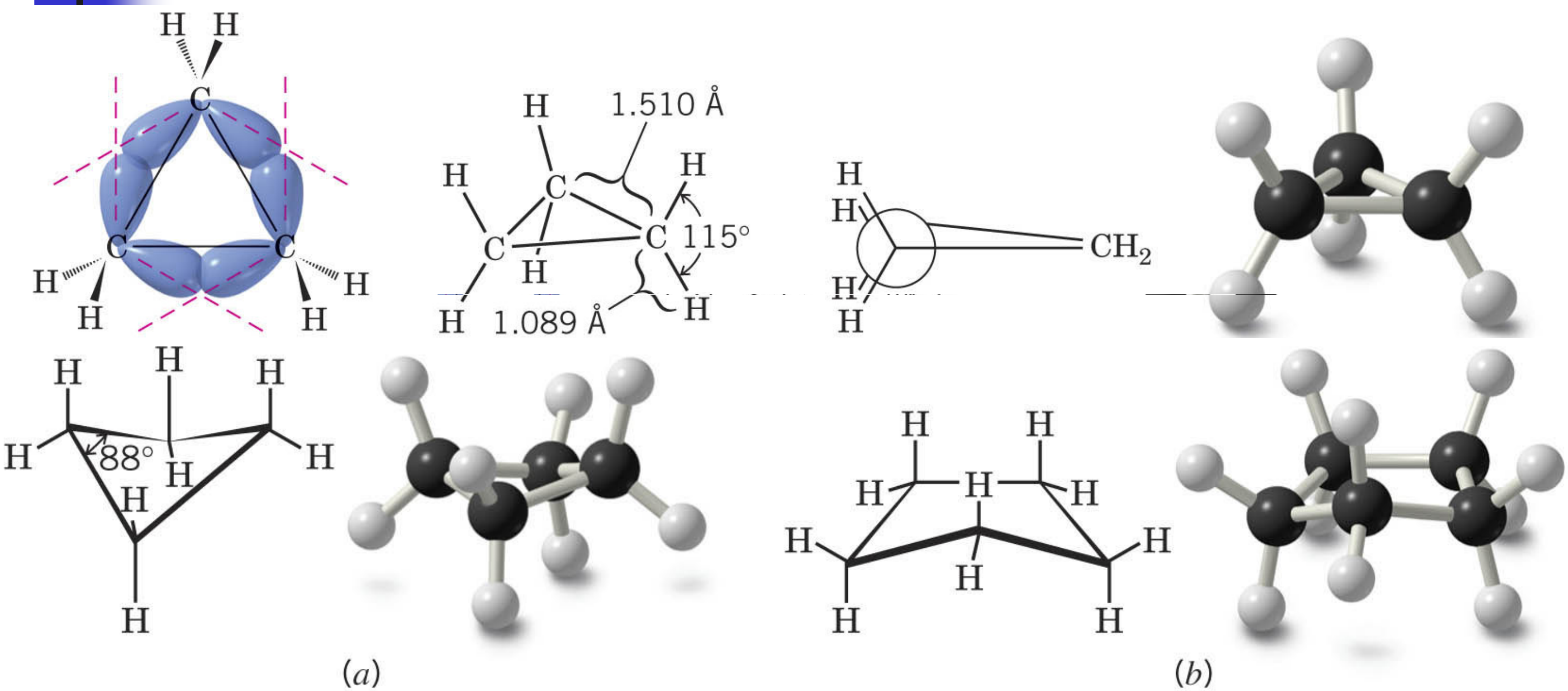
What is the correct name for the following cycloalkane?



1-bromo-3-ethylcyclohexane

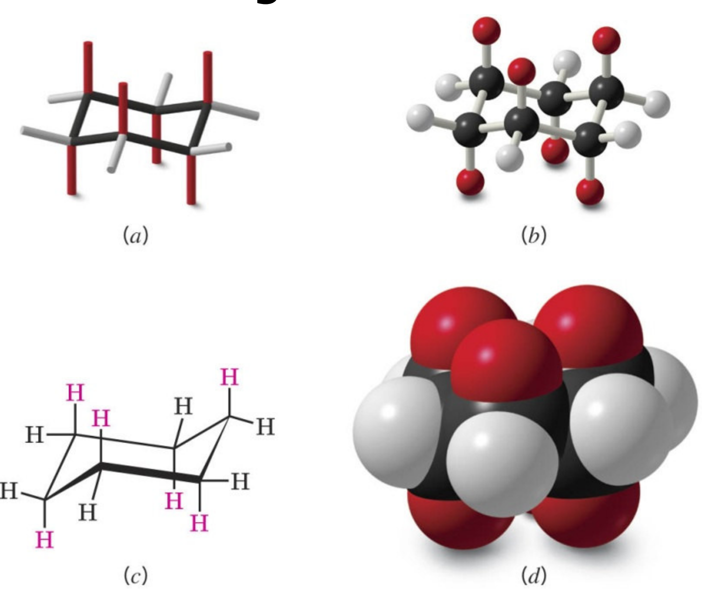
The Origin of Ring Strain in Cyclopropane and Cyclobutane

Angle Strain and Tortional Strain



- Cyclopentane has little angle strain in the planar form but bends to relieve some tortional strain

- Conformations of Cyclohexane
  - The chair conformation has no ring strain
    - All bond angles are 109.5º and all C-H bonds are



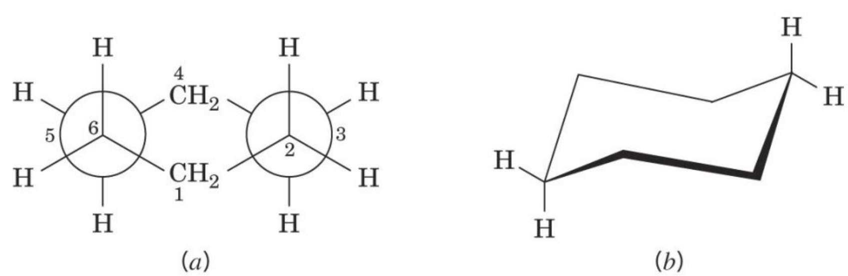
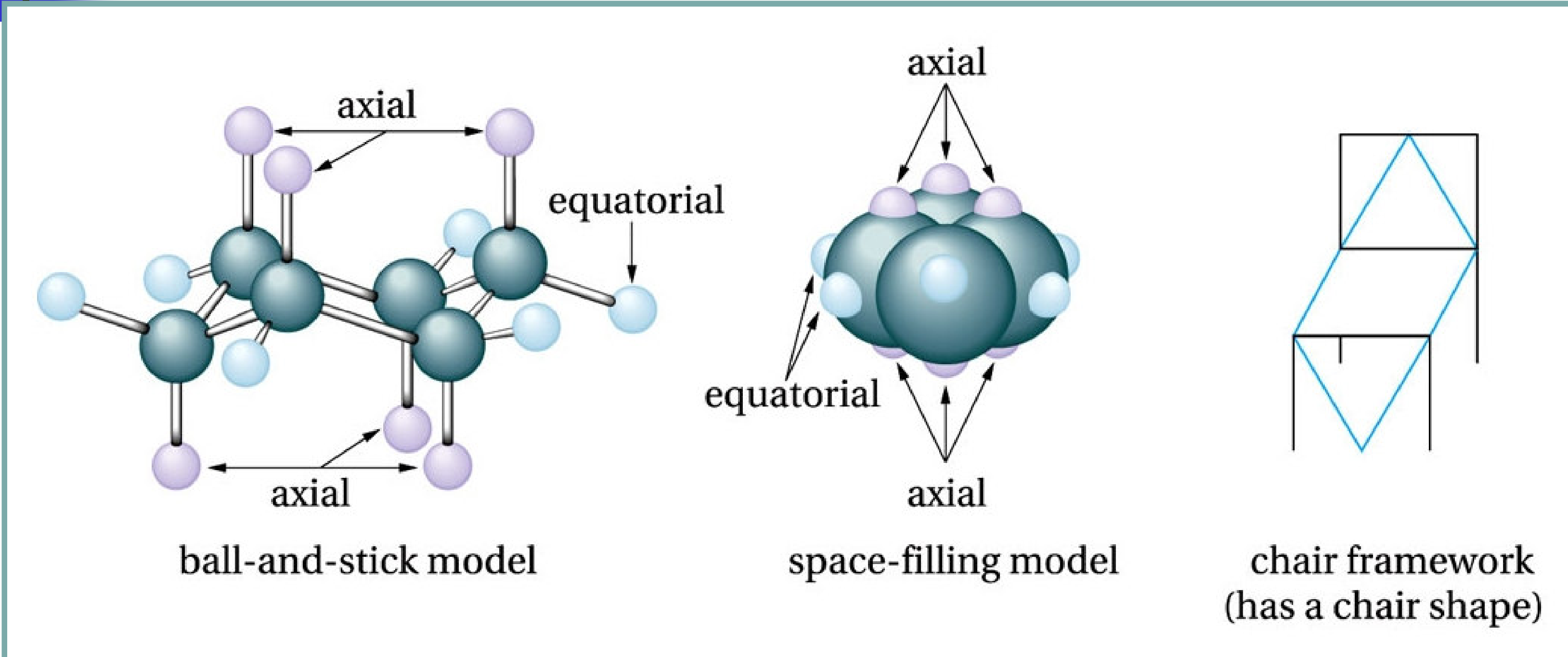


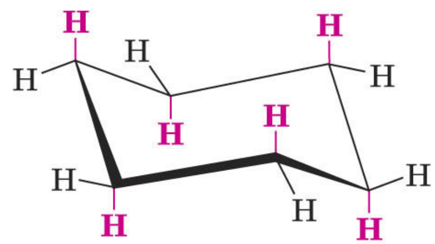
Figure 2.6 The chair conformation of cyclohexane



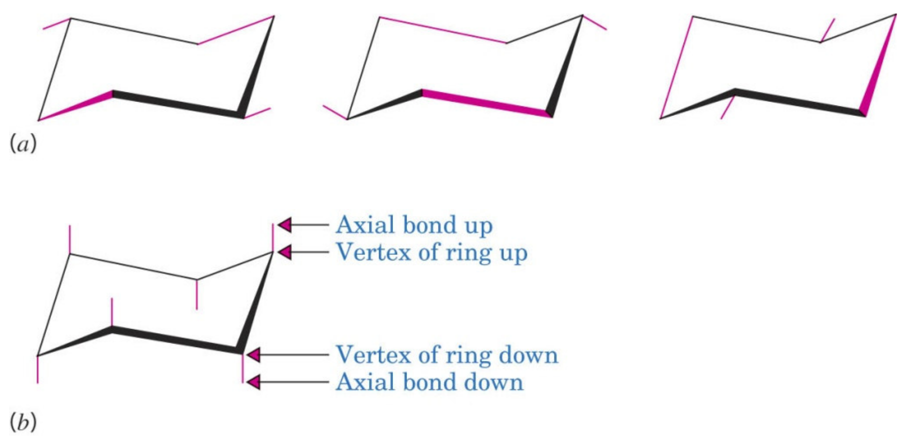
- animation

Substituted Cyclohexanes: Axial and Equatorial Hydrogen Atoms

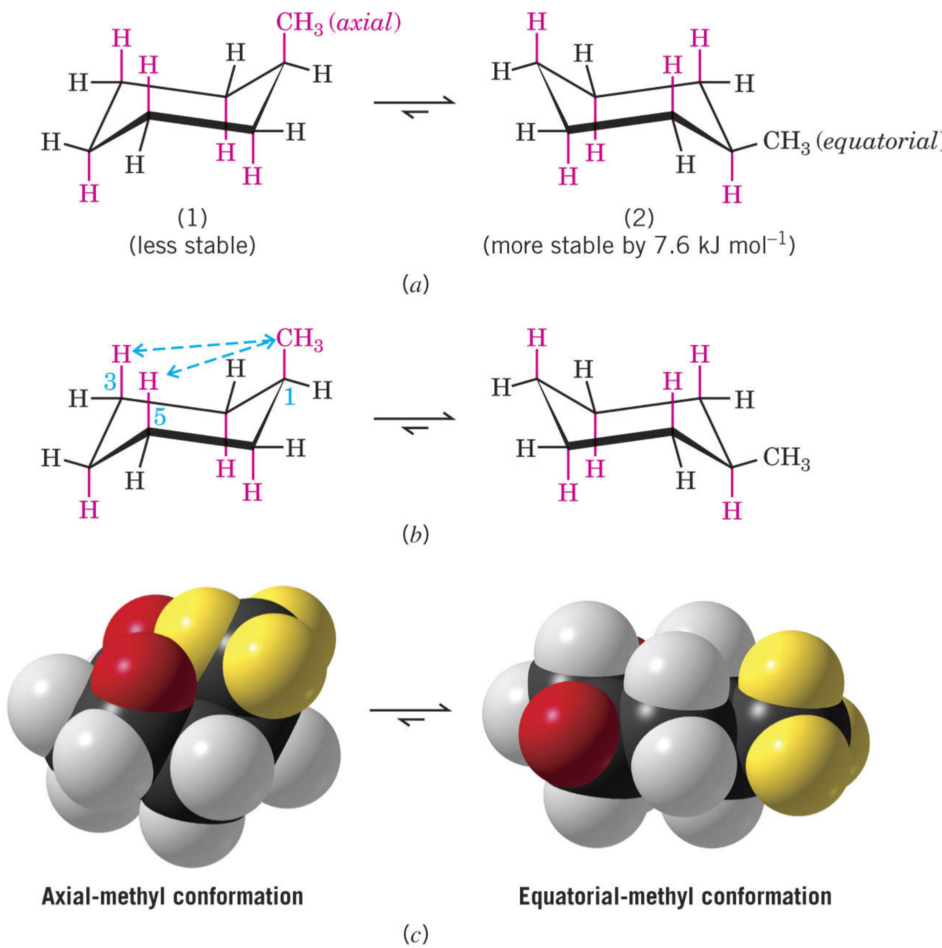
- Axial hydrogens are perpendicular to the average plane of the ring
- Equatorial hydrogens lie around the perimeter of the ring



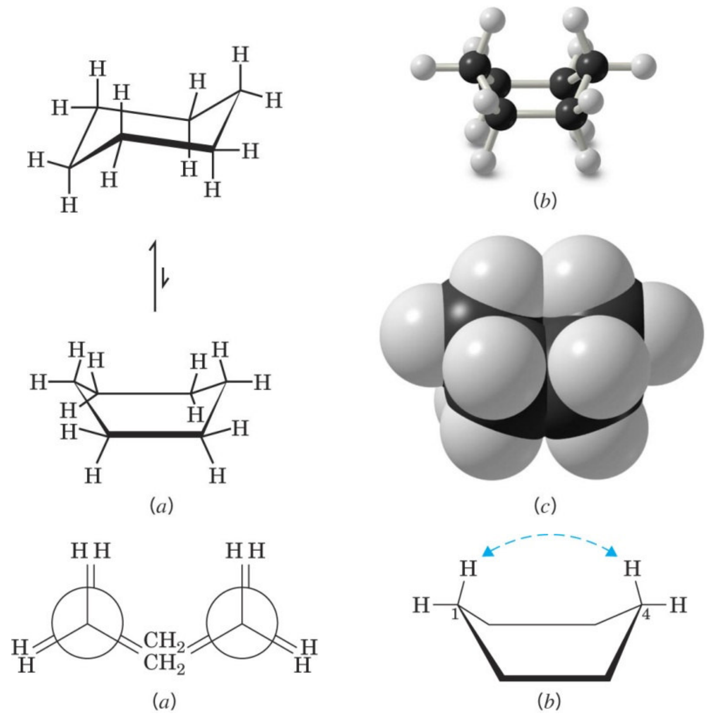
- The C-C bonds and equatorial C-H bonds are all drawn in sets of parallel lines
  - The axial hydrogens are drawn straight up and down



- Methyl cyclohexane is more stable with the methyl equatorial
  - An axial methyl has an unfavorable 1,3-diaxial interaction with axial C-H bonds 2 carbons away
  - A 1,3-diaxial interaction is the equivalent of 2 gauche butane interactions



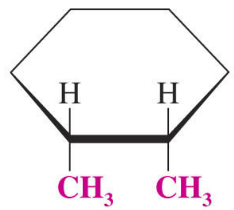
- The boat conformation is less stable because of flagpole interactions and tortional strain along the bottom of the boat



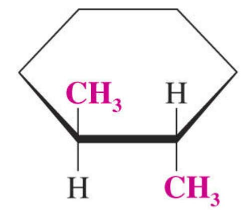
- The twist conformation is intermediate in stability between the boat and the chair conformation

Cis-Trans Isomerism in Cycloalkanes

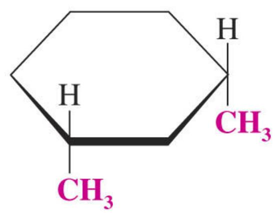
- # Disubstitued Cycloalkanes
  - Can exist as pairs of cis-trans stereoisomers
    - Cis: groups on same side of ring
    - Trans: groups on opposite side of ring



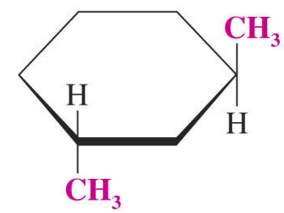
cis-1,2-Dimethylcyclohexane



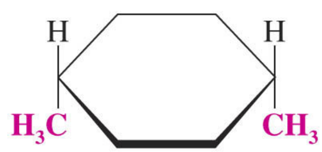
trans-1,2-Dimethylcyclohexane



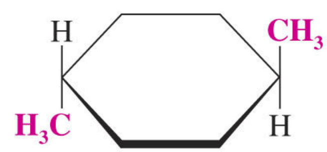
cis-1,3-Dimethylcyclohexane



trans-1,3-Dimethylcyclohexane

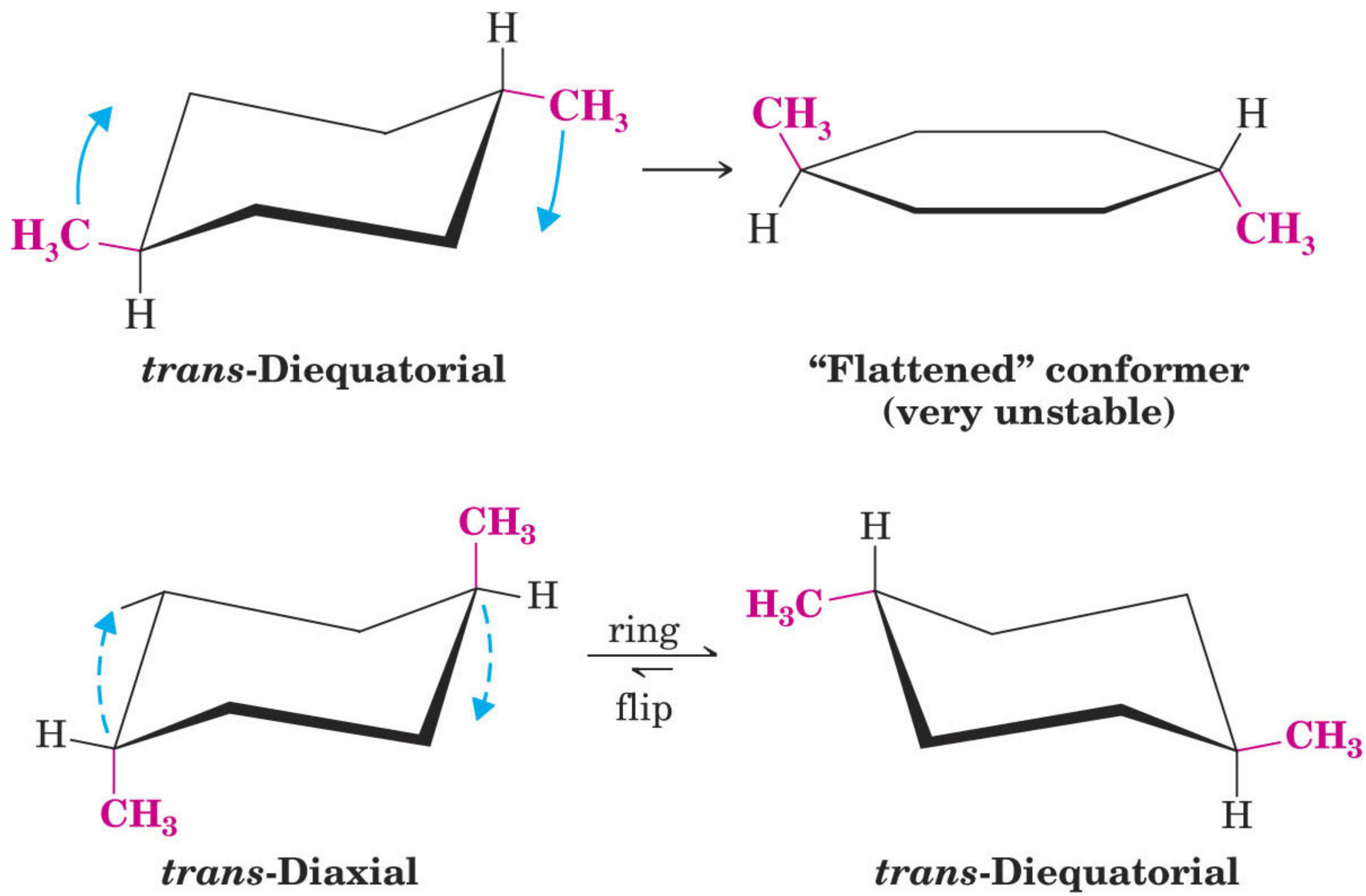


cis-1,4-Dimethylcyclohexane

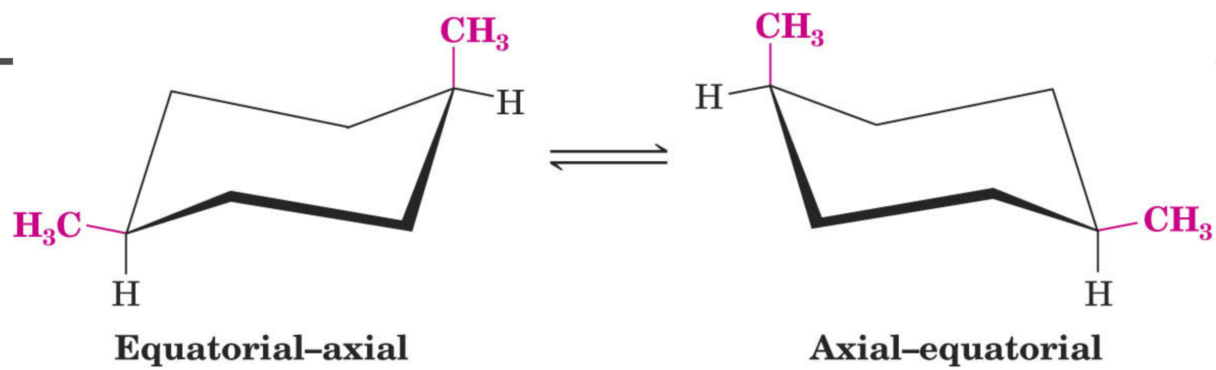


trans-1,4-Dimethylcyclohexane

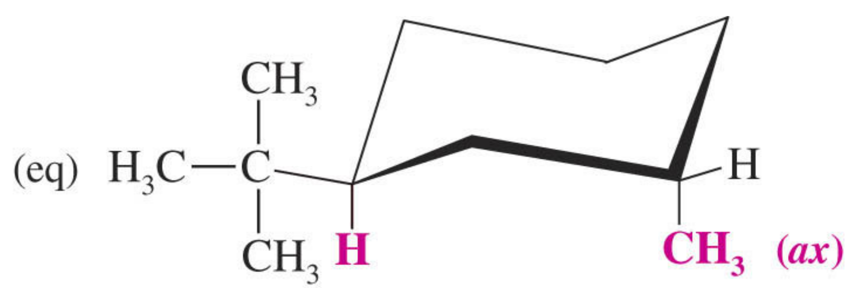
- *Trans*-1,4-dimethylcylohexane prefers a *trans*-diequatorial conformation



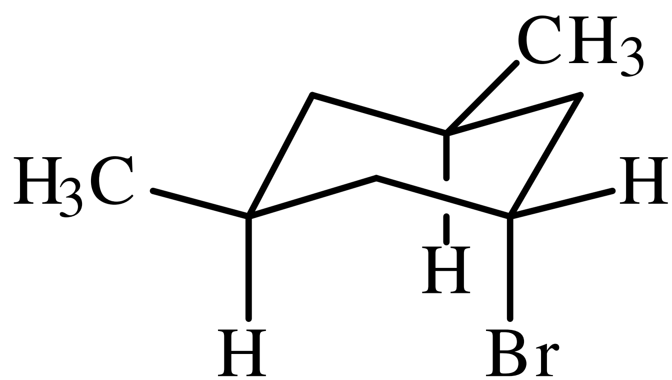
- *Cis*-1,4-dimethylcyclohexane exists in an axial-equatorial conformation



- A very large *tert*-butyl group is required to be in the more stable equatorial position



Consider this chair conformation

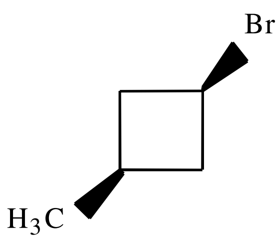


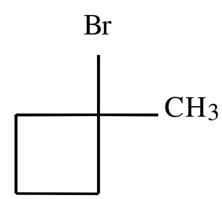
When the ring flips,

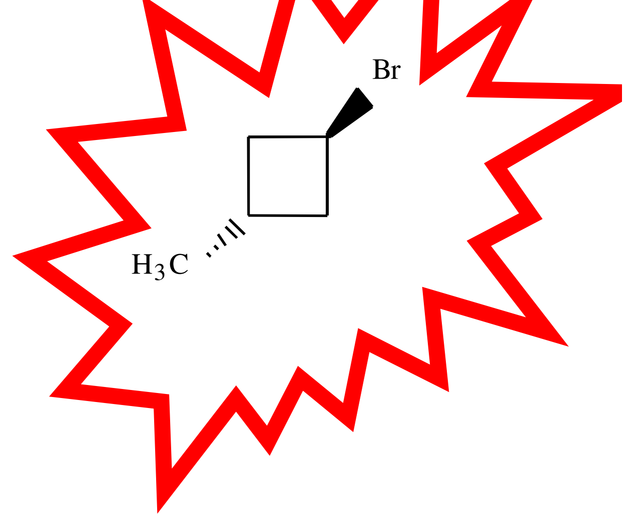
a. the bromine becomes axial and the methyls become equatorial.
b. all three substituents become equatorial.
$\boxed{\text{c. the bromine becomes equatorial and the methyls become axial.}}$
d. the ring opens up.
e. one methyl becomes axial, one becomes equatorial, and the bromine becomes equatorial.

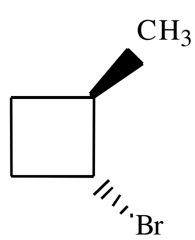
examples

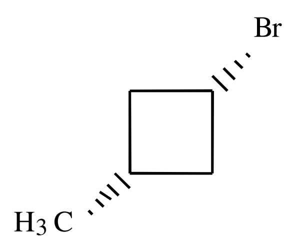
- *Trans*-1-bromo-3-methylcyclobutane is represented by which structure below?



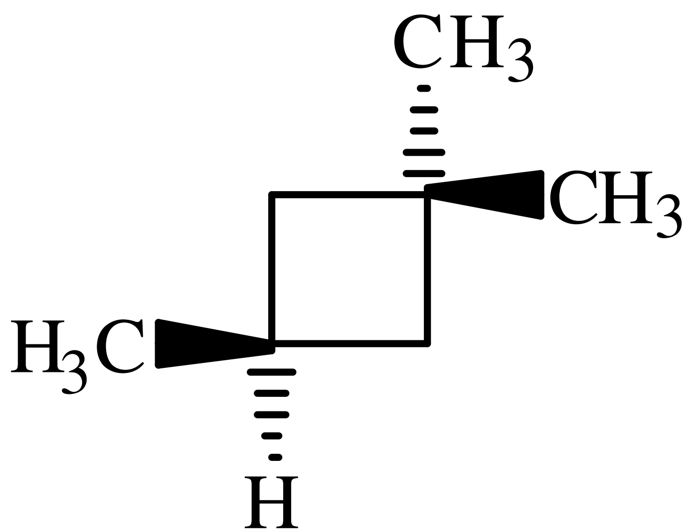








The correct IUPAC name for



1,3,3-trimethylcyclobutane.

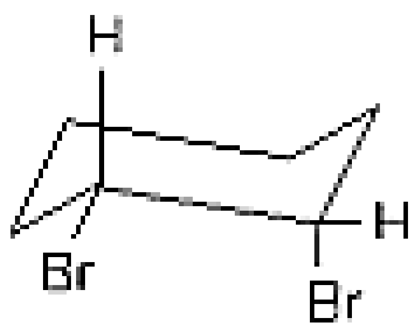
cis-1,3,3-trimethylcyclobutane.

trans-1,3,3-trimethylcyclobutane.

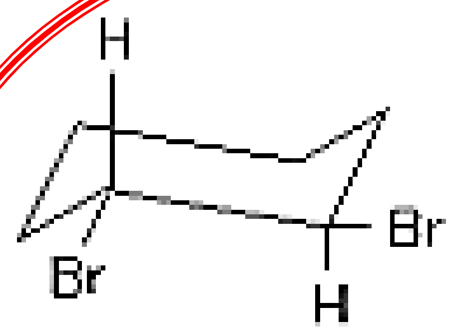
1,1,3-trimethylcyclobutane.

2,2,4-trimethylcyclobutane.

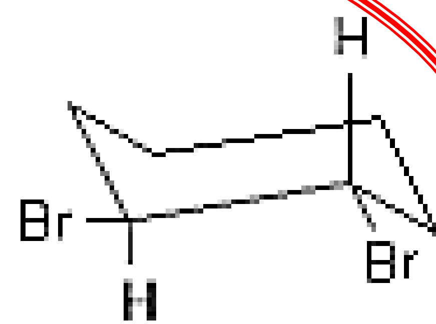
trans-1,2-Dibromocyclohexane is represented by structure(s):



I



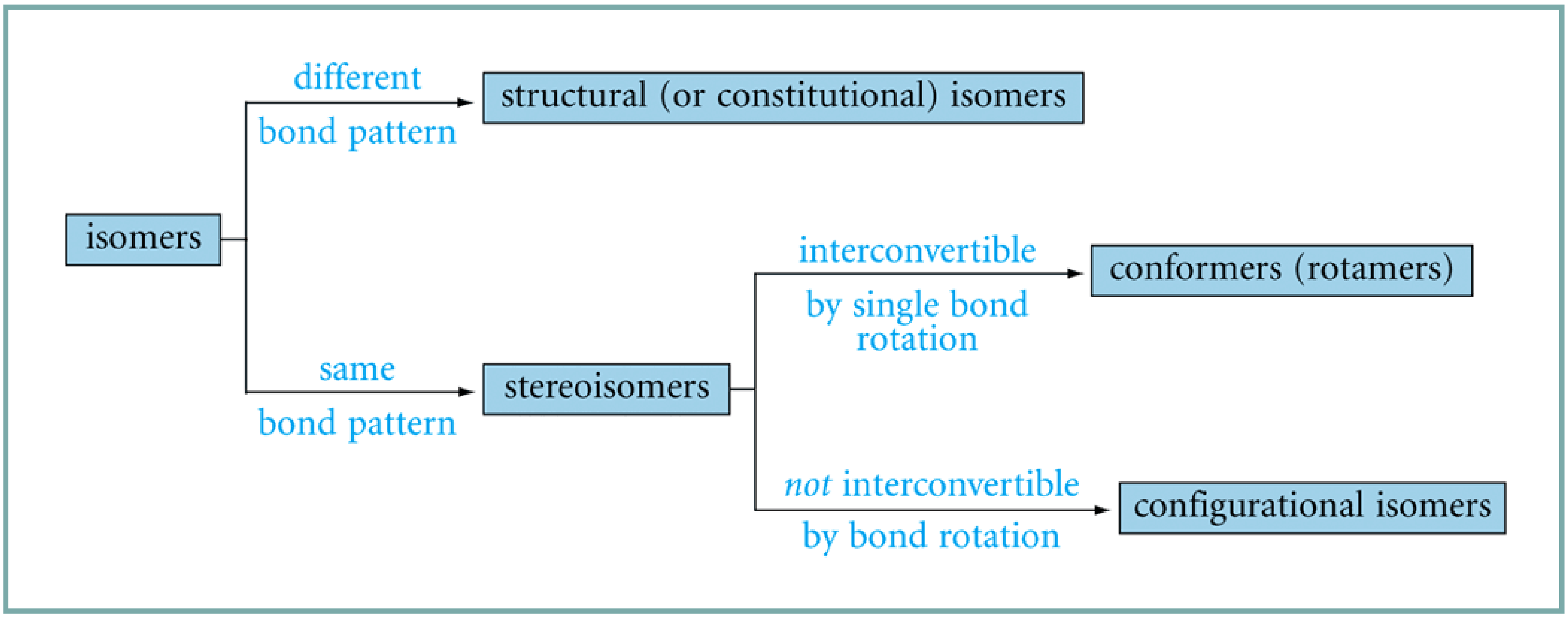
II



III

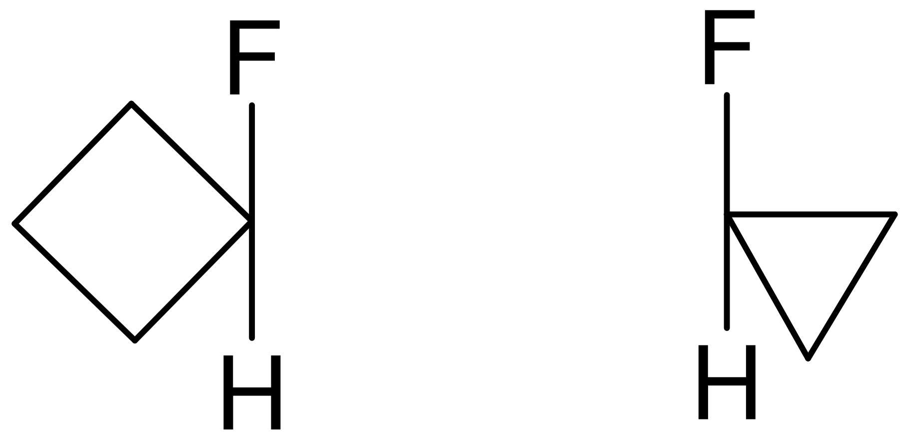
2.11 Summary of Isomerism

Figure 2.7 The relationships of the various types of isomers



Examples

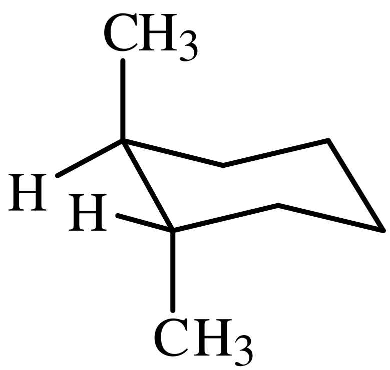
The molecules shown are:



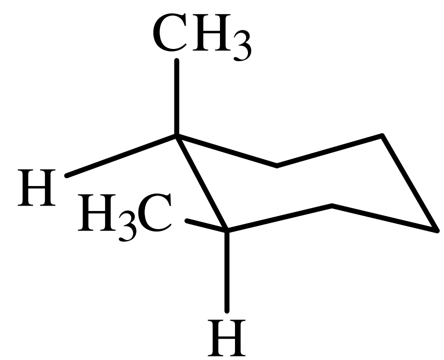
Not Isomers

Different compounds

The compounds represented by the structures



and



are

a. structural isomers. **b.** identical.

c. *cis-trans* isomers.

d. conformers. **e.** constitutional isomers.

2.12 Reactions of Alkanes

2.12.a Oxidation & Combustion;
Alkanes as Fuels

Inertness of Alkanes

- Alkanes
  - All bonds are single, covalent, and nonpolar.
  - Do not react with most common acids, bases, or oxidizing and reducing agents.
  - Can be used as solvents.
  - Do react with oxygen and halogens.

Alkanes are fuels;

- Alkanes burn in air if ignited.
  - Complete combustion gives carbon dioxide and water; less complete combustion gives carbon monoxide or other less oxidized forms of carbon.
- Alkanes react with **halogens** (chlorine or bromine) in a reaction initiated by heat or light.
  - One or more hydrogens can be replaced by halogens.
  - This **substitution reaction** occurs by a **free-radical chain mechanism**.

Oxidation & Combustion

- Combustion of hydrocarbons is an **oxidation reaction** in which **C-H** bonds are replaced with **C-O** bonds.

General Reaction

$$C_nH_{2n+2} + (\frac{3n+1}{2})O_2 \xrightarrow{spark} nCO_2 + (n+1)H_2O$$

- The reaction is exothermic: the basis for the use of alkanes for heat and for power.
- Once initiated by spark or flame, the reaction proceeds spontaneously and exothermally.
- Alkanes burned to CO_2 and H_2O with excess O_2.

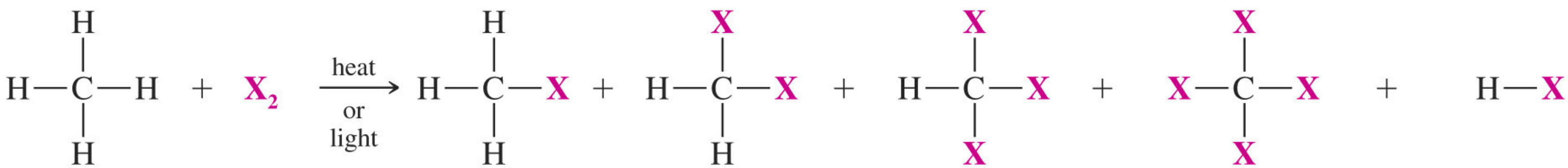
Insufficient O_2

- Partial oxidation may occur
  - For incomplete combustion of methane:
  - CO, C, CH_2O might be formed

2.12.b Halogenation of Alkanes

The Reactions of Alkanes with Halogens

- Alkanes undergo substitution reactions with halogens such as fluorine, bromine and chlorine in the presence of heat or light

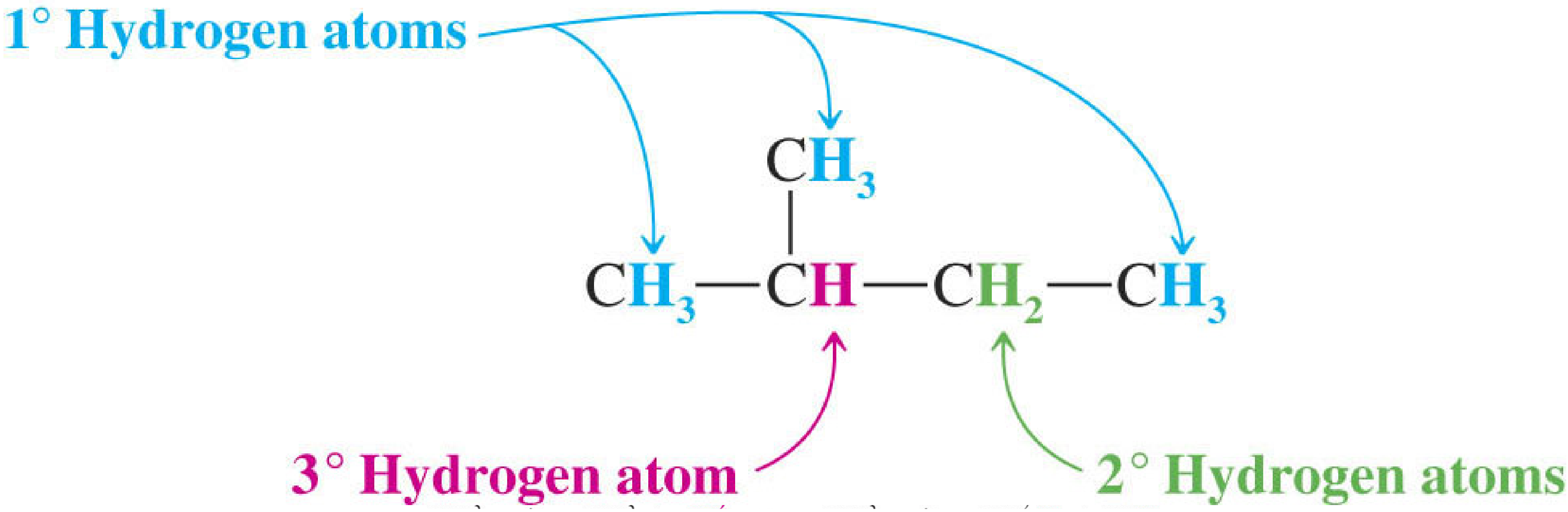


Methane **Halogen** **Halomethane** **Dihalomethane** **Trihalomethane** **Tetrahalomethane** **Hydrogen halide**

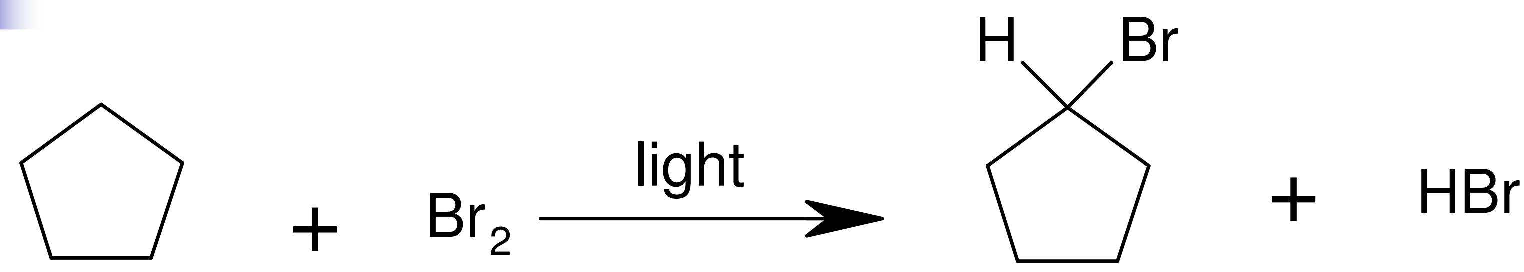
X = F, Cl, or Br

(The sum of the number of moles of each halogenated methane produced equals the number of moles of methane that reacted.)

- Multiple Substitution Reactions versus Selectivity
  - Radical halogenation can yield a mixture of halogenated compounds because all hydrogen atoms in an alkane are capable of substitution
    - In the reaction above all degrees of methane halogenation will be seen
  - Monosubstitution can be achieved by using a large excess of the alkane
    - A large excess of methane will lead to predominantly monohalogenated product and excess unreacted methane


1° Hydrogen atoms
CH3
CH3—CH—CH2—CH3
3° Hydrogen atom
2° Hydrogen atoms

EXAMPLES



- With Unsubstituted cycloalkanes, where all H's are equivalent, a single pure organic product can be obtained.

- How many monobromo products can be obtained from the bromination of cyclopentane?

  a. 1 **b.** 2 **c.** 3 **d.** 4 **e.** 5

- How many isomeric dichloro products can be obtained from the chlorination of cyclopropane?

  a. 1 **b.** 2 **c.** 3 **d.** 4 **e.** 5

2.13 The Free-Radical Chain Mechanism of Halogenation

Chlorination of Methane: Mechanism of Reaction

- The reaction mechanism has three distinct aspects:
  Chain initiation, chain propagation and chain termination
- Chain initiation
  - Chlorine radicals form when the reaction is subjected to heat or light
  - Chlorine radicals are used in the chain propagation steps below

Chain Initiation

$$\textit{Step 1} \quad Cl_2 \xrightarrow[\text{or light}]{\text{heat}} 2\,Cl\cdot$$

Chain Propagation

$$\textit{Step 2} \quad CH_4 + Cl\cdot \longrightarrow CH_3\cdot + H{-}Cl$$

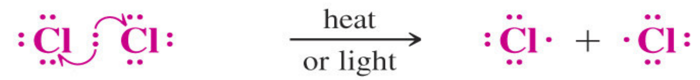
$$\textit{Step 3} \quad CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

- Chain propagation
  - A chlorine radical reacts with a molecule of methane to generate a methyl radical
  - A methyl radical reacts with a molecule of chlorine to yield chloromethane and regenerate chlorine radical
  - A chlorine radical reacts with another methane molecule, continuing the chain reaction
  - A single chlorine radical can lead to thousands of chain propagation cycles

The entire mechanism is shown below

$$CH_4 + Cl_2 \xrightarrow[\text{or light}]{\text{heat}} CH_3Cl + HCl$$

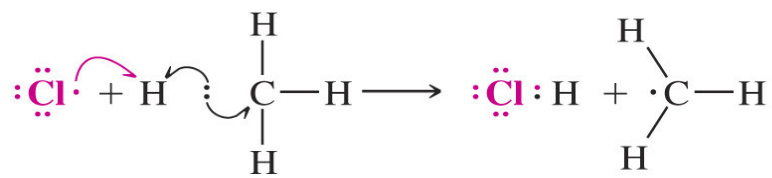
Step 1



Under the influence of heat or light a molecule of chlorine dissociates; each atom takes one of the bonding electrons.

This step produces two highly reactive chlorine atoms.

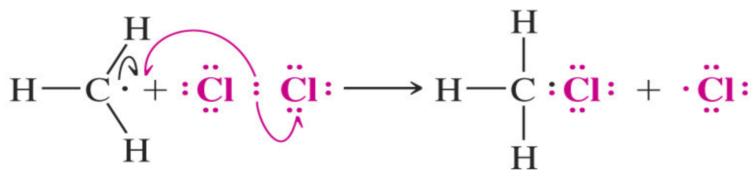
Step 2



A chlorine atom abstracts a hydrogen atom from a methane molecule.

This step produces a molecule of hydrogen chloride and a methyl radical.

Step 3



A methyl radical abstracts a chlorine atom from a chlorine molecule.

This step produces a molecule of methyl chloride and a chlorine atom. The chlorine atom can now cause a repetition of step 2.

- Chain reaction: a stepwise mechanism in which each step generates the reactive intermediate that causes the next cycle of the reaction to occur
- Chain termination
  - Occasionally the reactive radical intermediates are quenched by reaction pathways that do not generate new radicals
  - The reaction of chlorine with methane requires constant irradiation to replace radicals quenched in chain-terminating steps