

*Organic Chemistry*, 7<sup>th</sup> Edition  
L. G. Wade, Jr.

# Chapter 3

## Structure and Stereochemistry of Alkanes

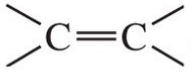
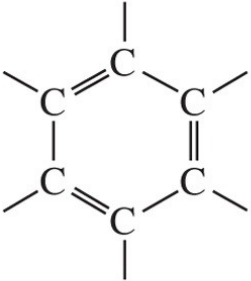
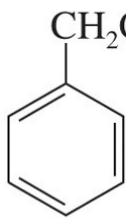
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# Hydrocarbons

**Hydrocarbons are molecules that are made of carbon and hydrogen ONLY.**

**TABLE 3-1**

Hydrocarbon Classifications

Compound Type	Functional Group	Example
alkanes	none (no double or triple bonds)	$\text{CH}_3\text{—CH}_2\text{—CH}_3$ , propane
alkenes	 double bond	$\text{CH}_2=\text{CH—CH}_3$ , propene
alkynes	$\text{—C}\equiv\text{C—}$ triple bond	$\text{H—C}\equiv\text{C—CH}_3$ , propyne
aromatics	benzene ring 	 ethylbenzene

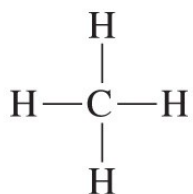
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# Alkanes

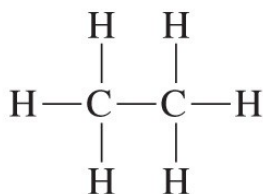
- General formula:  $C_nH_{2n+2}$
- Found in everything from natural gas to petroleum.
- The smaller alkanes have very low boiling points (b.p.) therefore they are gases.

	$CH_4$	$C_2H_6$	$C_3H_8$
b.p.	$-160^\circ C$	$-89^\circ C$	$-42^\circ C$

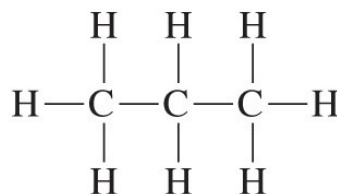
# Alkane Examples



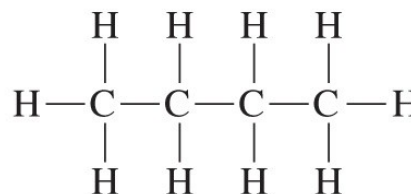
methane,  $\text{CH}_4$



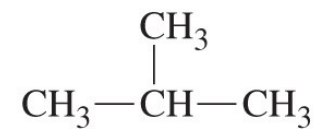
ethane,  $\text{C}_2\text{H}_6$



propane,  $\text{C}_3\text{H}_8$



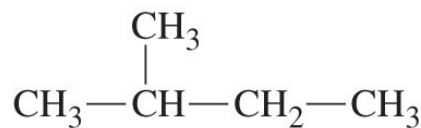
butane,  $\text{C}_4\text{H}_{10}$



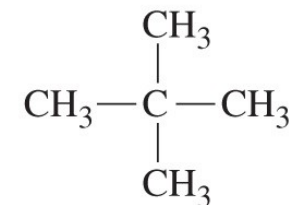
isobutane,  $\text{C}_4\text{H}_{10}$



pentane,  $\text{C}_5\text{H}_{12}$



isopentane,  $\text{C}_5\text{H}_{12}$



neopentane,  $\text{C}_5\text{H}_{12}$

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# Small Alkanes ( $C_nH_{2n+2}$ )

- Methane  $CH_4$
- Ethane  $CH_3 \blacksquare CH_3$
- Propane  $CH_3 \blacksquare CH_2 \blacksquare CH_3$

Butane: C<sub>4</sub>H<sub>10</sub>

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>     *n*-butane

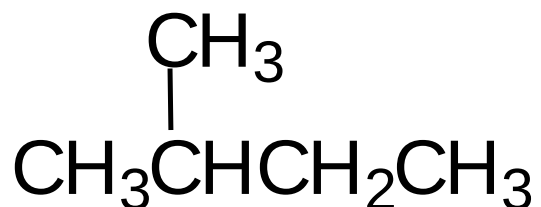
CH<sub>3</sub>  
|  
CH<sub>3</sub>CHCH<sub>3</sub>     *iso*-butane

***Constitutional isomers*** are compounds with the same molecular formula but the carbons are connected differently.

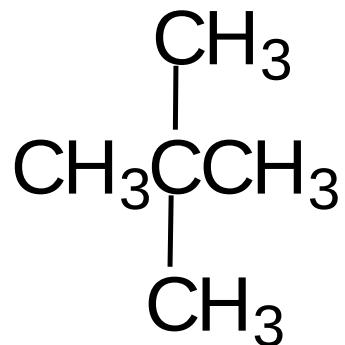
# Pentanes: C<sub>5</sub>H<sub>12</sub>



*n*-pentane



*iso*-pentane



*neo*-pentane

# IUPAC

- International Union of Pure and Applied Chemistry
- Common names kept: **methane**, **ethane**, **propane**, **butane**.
- Alkanes: suffix “-ane” will be used after the number of carbons.
  - Example: An alkane with 5 carbons is “penta” for five and the suffix “-ane”:  
**pentane**



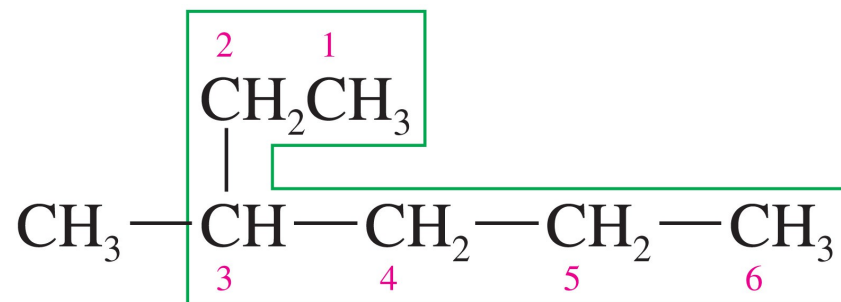
# IUPAC Rules

- **Rule 1:** Find the longest continuous chain of carbon atoms, and use the name of this chain as the base name of the compound.
- **Rule 2:** Number the longest chain, beginning with the end of the chain nearest a substituent.
- **Rule 3:** Name the groups attached to the longest chain as alkyl groups. Give the location of each alkyl group by the number of the main chain carbon atom to which it is attached.
- Write the alkyl groups in alphabetical order regardless of their position on the chain.

# Rule 1: Find the Longest Chain of Consecutive Carbons.

The longest chain is six carbons:

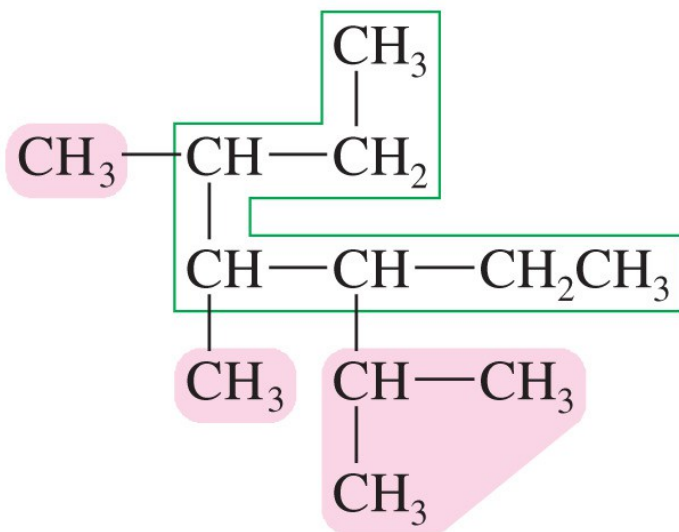
hexane



3-methylhexane

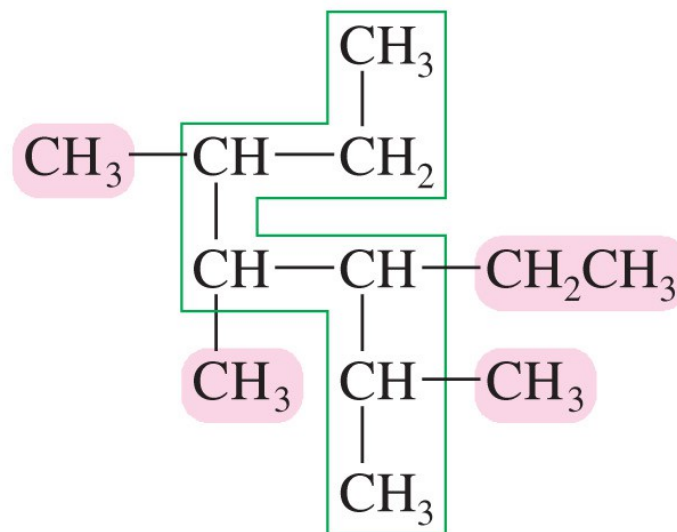
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# Main Chain



wrong

seven-carbon chain, but only three substituents



correct

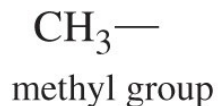
seven-carbon chain, four substituents

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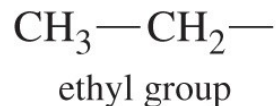
When there are two longest chains of equal length, use the chain with the greatest number of substituents.

# Common Alkyl Groups

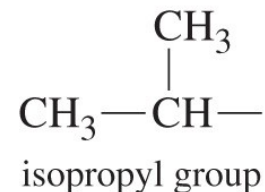
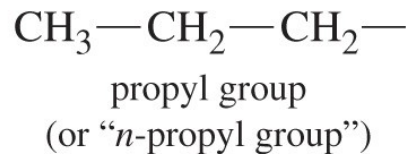
*One carbon*



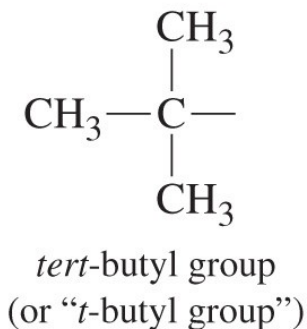
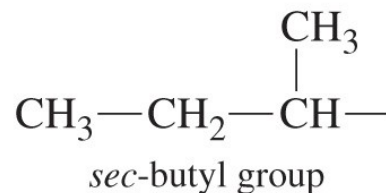
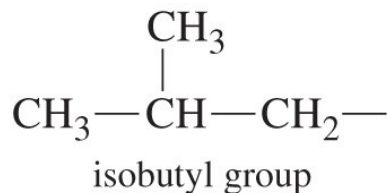
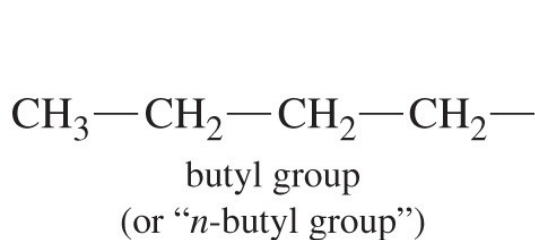
*Two carbons*



*Three carbons*



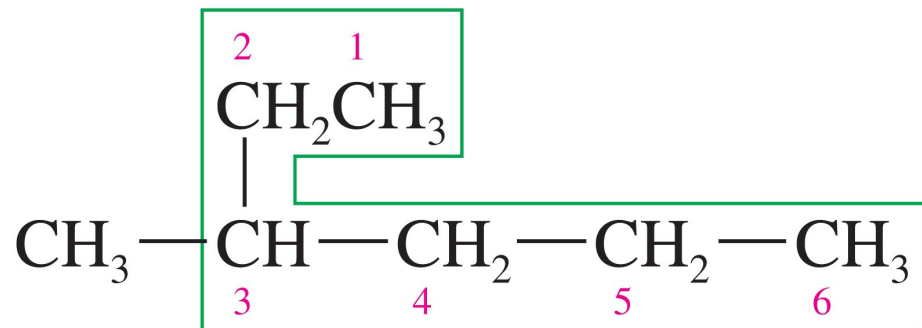
*Four carbons*



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# Rule 2: Number the Longest Chain.

Methyl is closest to this end of the main chain.



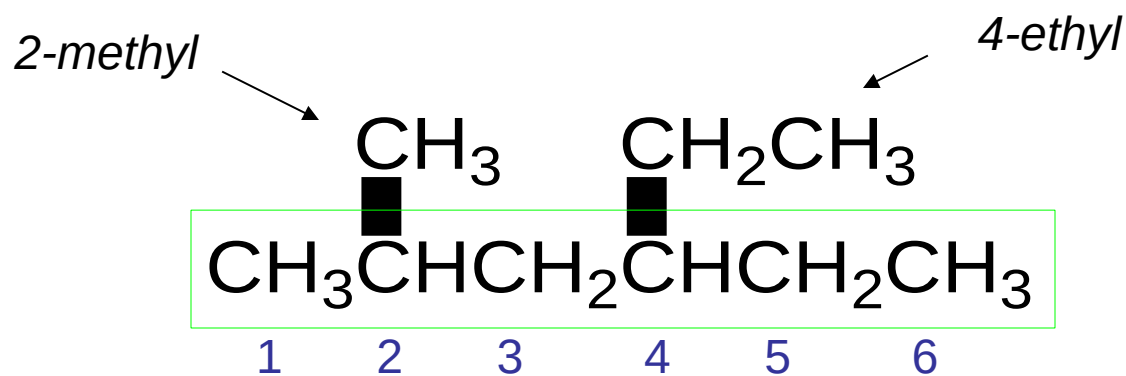
*3-methylhexane*

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Number the longest chain, beginning with the end of the chain nearest a substituent.

3-methylehexane

# Rule 3: Alkyl Substituents

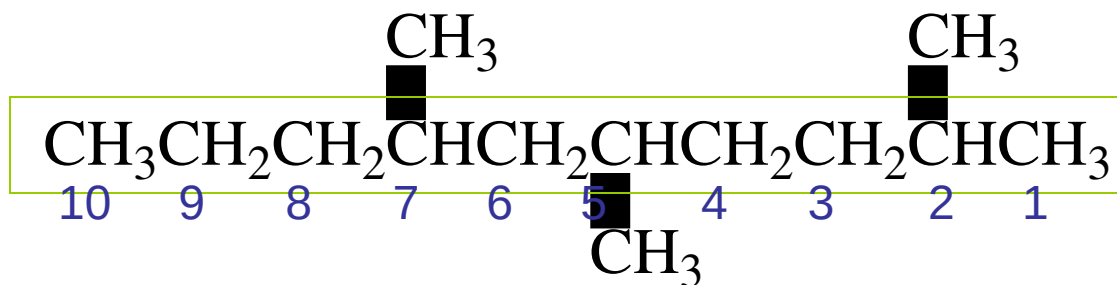


- Name the groups attached to the longest chain as alkyl groups.
- Give the location of each alkyl group by the number of the main chain carbon atom to which it is attached.
- Write the alkyl groups in alphabetical order regardless of their position on the chain.

4-ethyl-2-methylhexane

# Organizing Multiple Groups

- When two or more of the same substituents are present, use the prefixes *di-*, *tri-*, *tetra-*, etc. to avoid having to name the alkyl group twice.



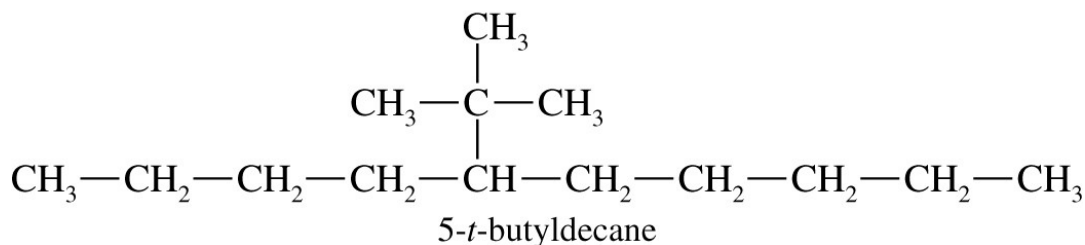
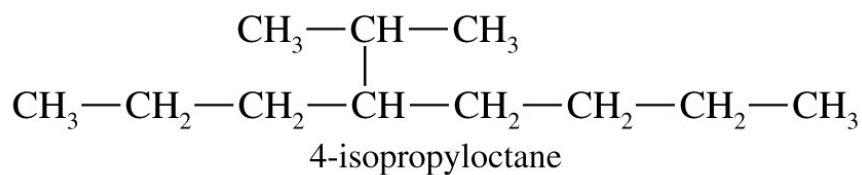
Three methyl groups at positions 2, 5, and 7

**2,5,7-trimethyldecane**

# Solved Problem 3-1

Give the structures of 4-isopropyloctane and 5-*t*-butyldecane.

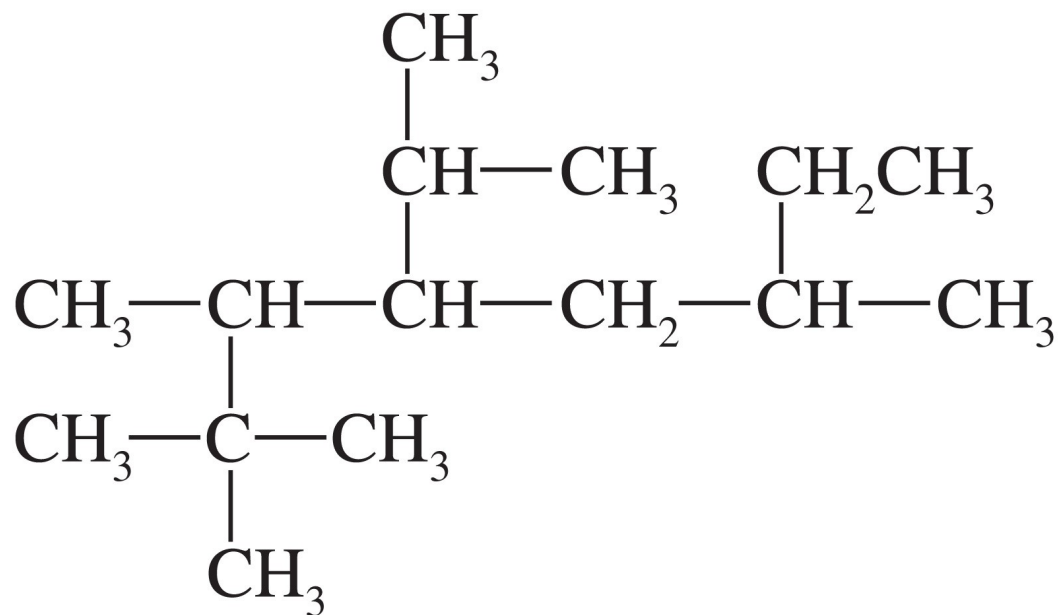
Solution: 4-Isopropyloctane has a chain of eight carbons, with an isopropyl group on the fourth carbon. 5-*t*-Butyldecane has a chain of ten carbons, with a *t*-butyl group on the fifth.





# Solved Problem 3-2

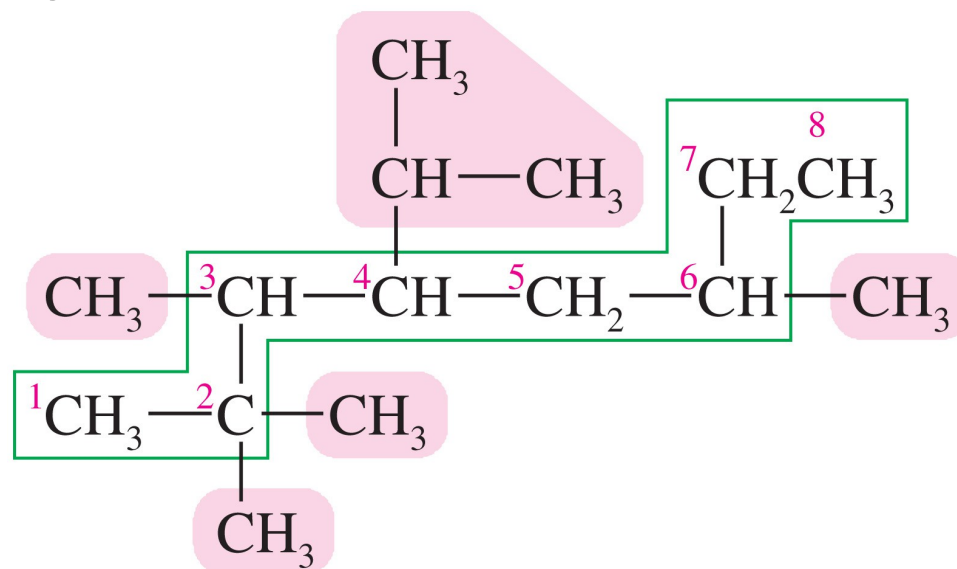
Give a systematic (IUPAC) name for the following compound.



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# Solved Problem 3-2: Solution

The longest carbon chain contains eight carbon atoms, so this compound is named as an octane. Numbering from left to right gives the first branch on C2; numbering from right to left gives the first branch on C3, so we number from left to right.

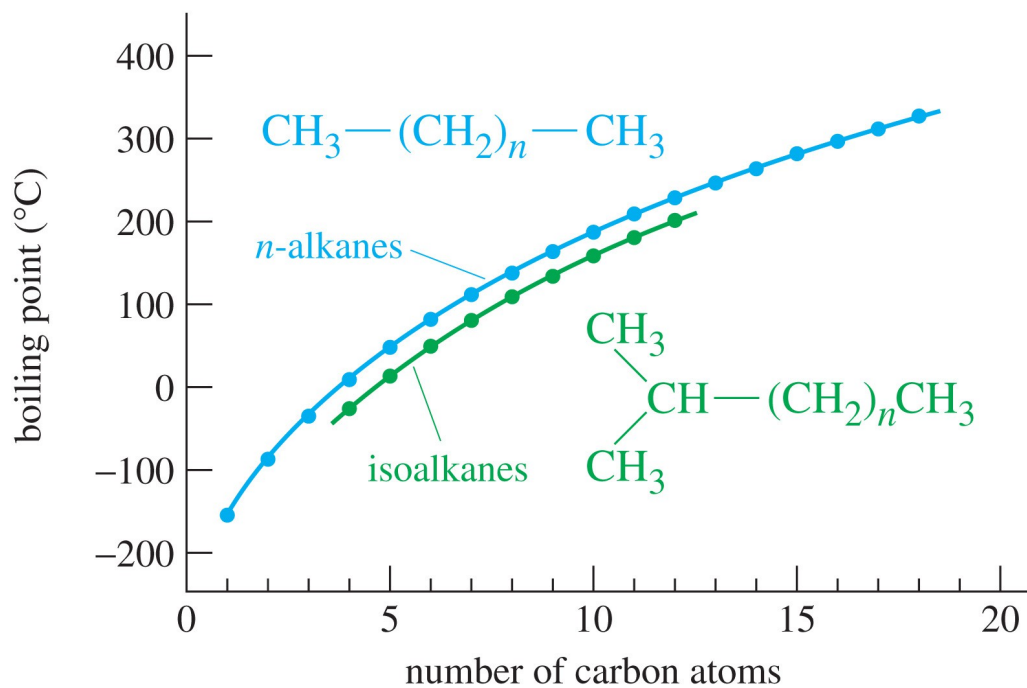


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**4-isopropyl-2,2,3,6-tetramethyloctane**

# Boiling Points of Alkanes

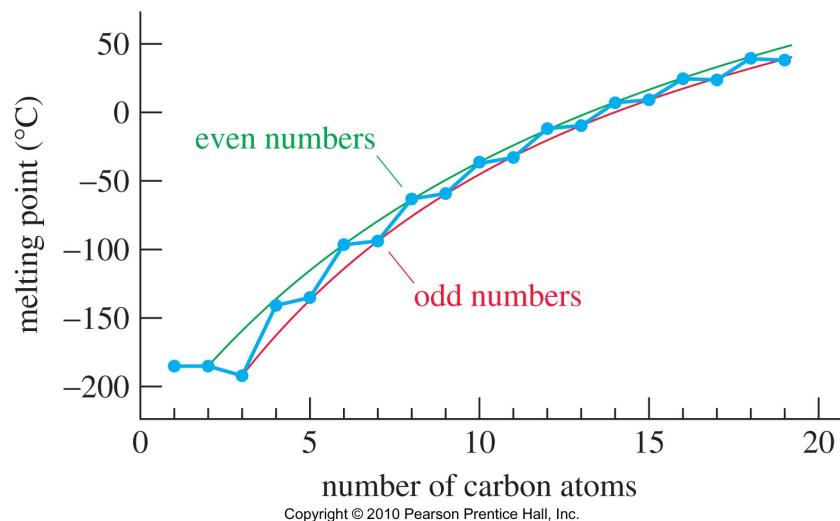
As the number of carbons in an alkane increases, the boiling point will increase due to the larger surface area and the increased van der Waals attractions.



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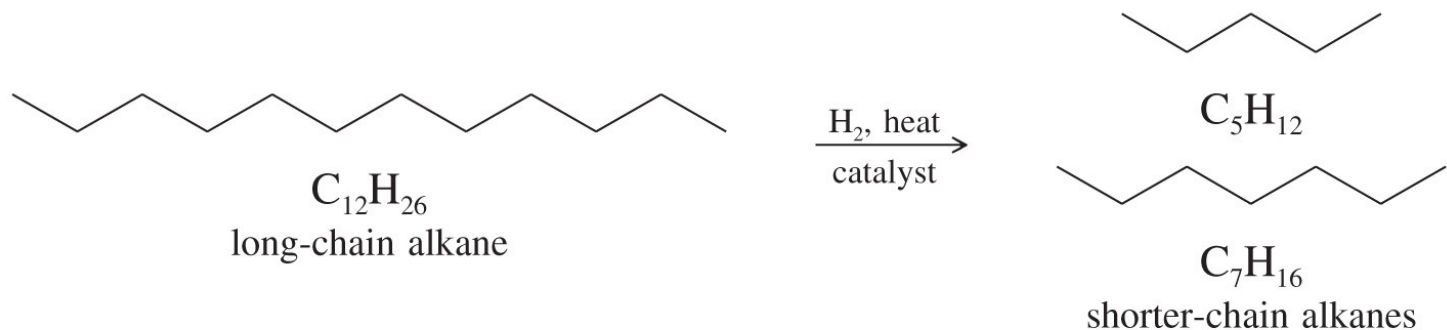
# Melting Points of Alkanes

- Melting points increase as the carbon chain increases.
- Alkanes with an even number of carbons have higher melting points than those with an odd number of carbons.
- Branched alkanes have higher melting points than unbranched alkanes.

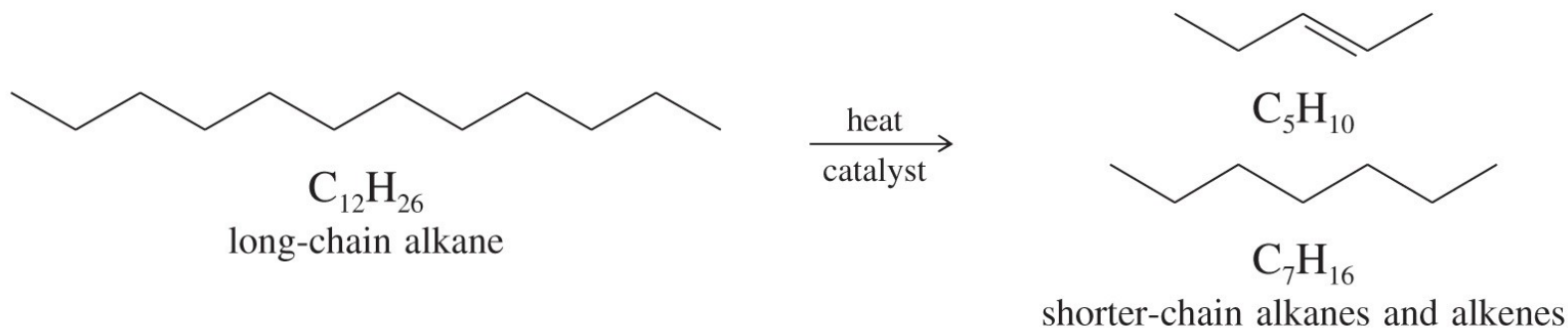


# Cracking and Hydrocracking

## *Catalytic hydrocracking*

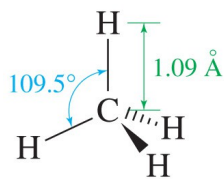


## *Catalytic cracking*

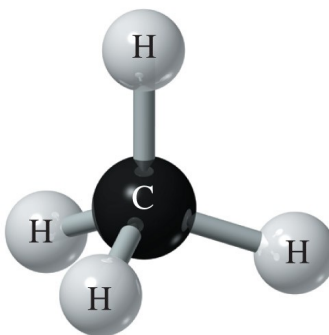


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# Methane Representations

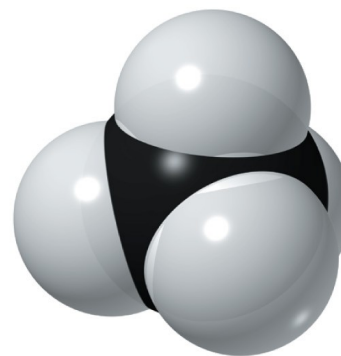


methane



methane

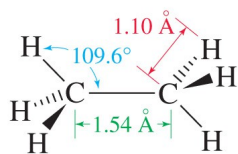
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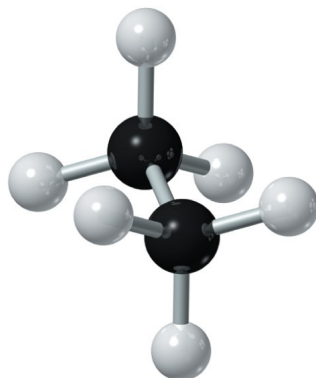
methane

- Tetrahedral
- $sp^3$  hybrid carbon with angles of  $109.5^\circ$ .

# Ethane Representations

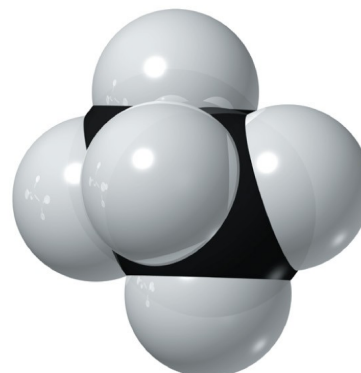


ethane



ethane

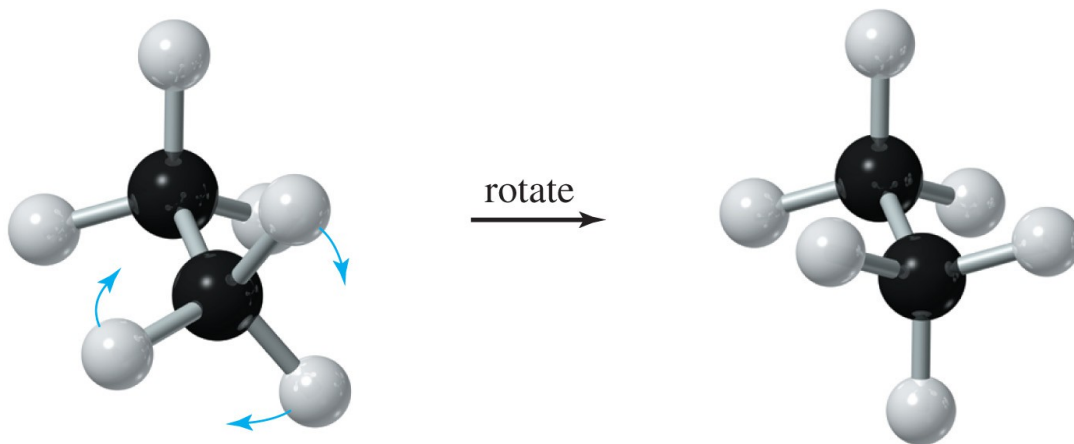
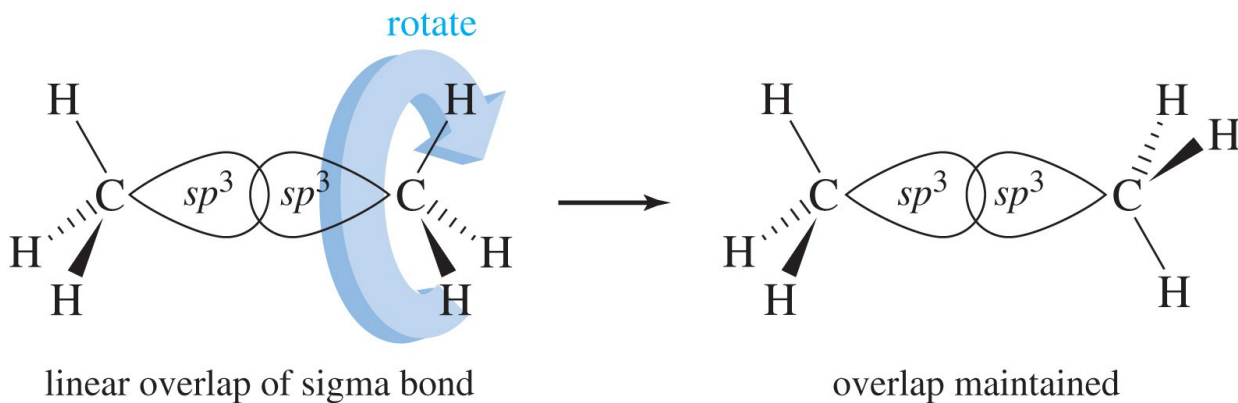
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ethane

- Two  $sp^3$  hybrid carbons.
- Rotation about the C—C sigma bond.
- **Conformations** are different arrangements of atoms caused by rotation about a single bond.

# Conformations of Ethane

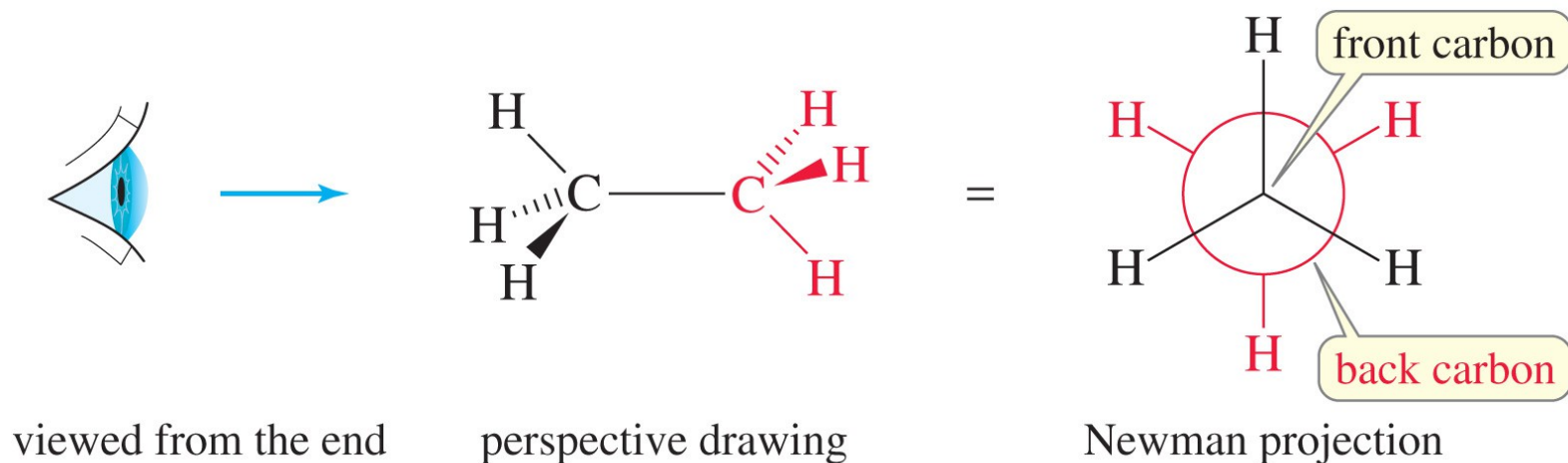


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Pure conformers cannot be isolated in most cases, because the molecules are constantly rotating through all the possible conformations.



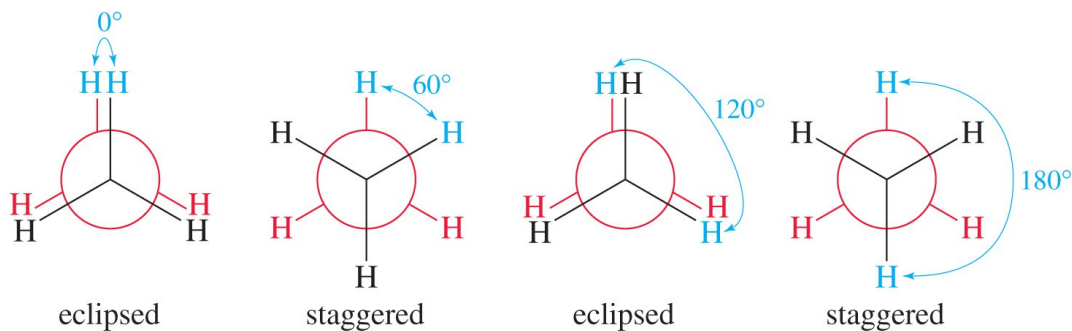
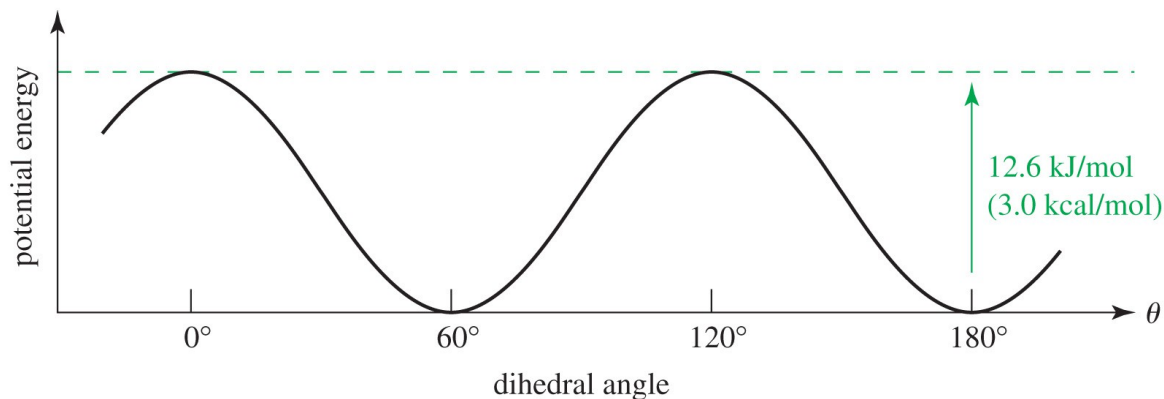
# Newman Projections



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The Newman projection is the best way to judge the stability of the different conformations of a molecule.

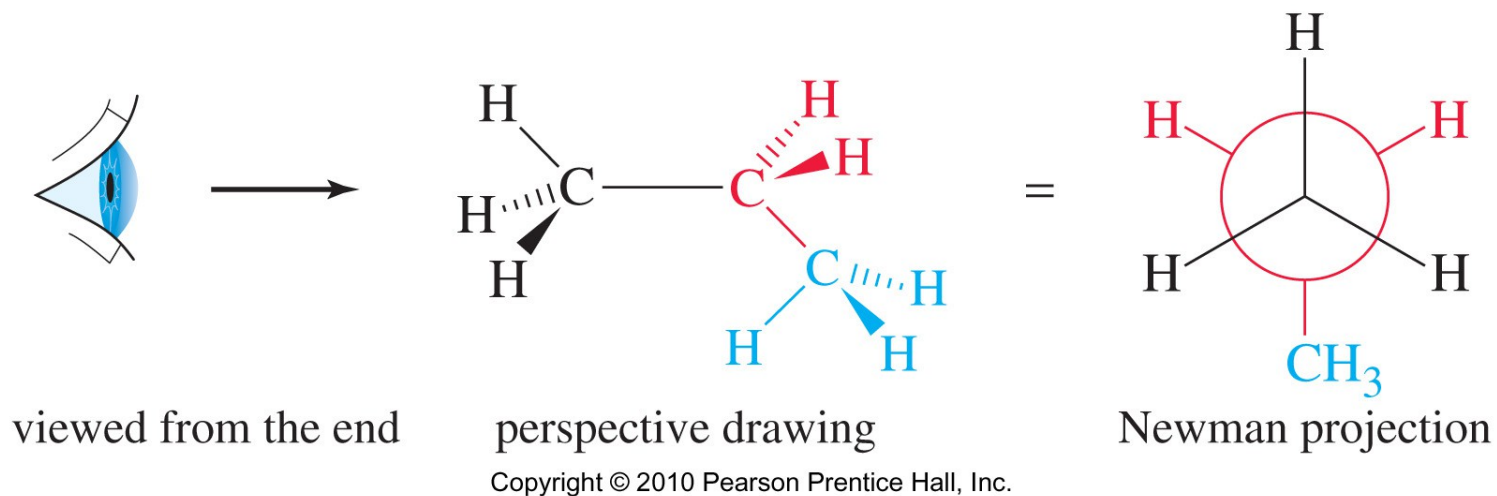
# Ethane Conformations



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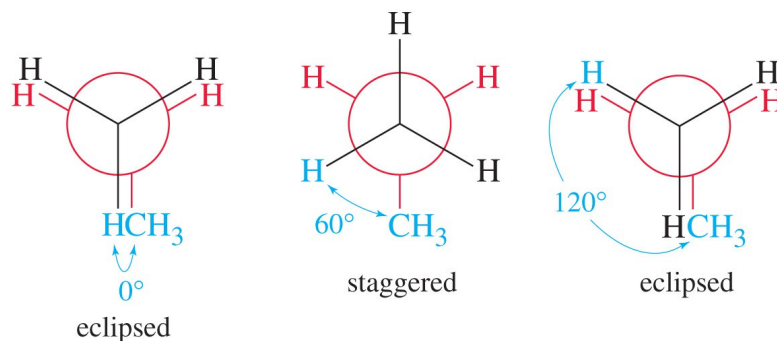
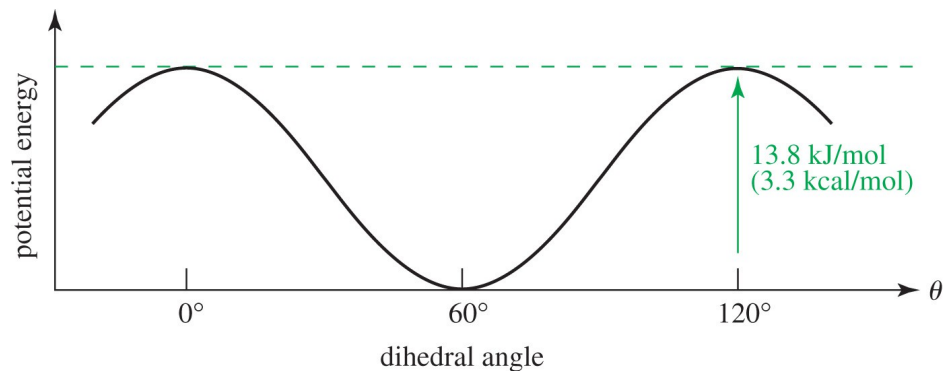
The torsional energy of ethane is lowest in the staggered conformation. The eclipsed conformation is about 3.0 kcal/mol (12.6 kJ/mol) higher in energy. At room temperature, this barrier is easily overcome, and the molecules rotate constantly.

# Propane Conformations



Propane is shown here as a perspective drawing and as a Newman projection looking down the C1—C2 bond.

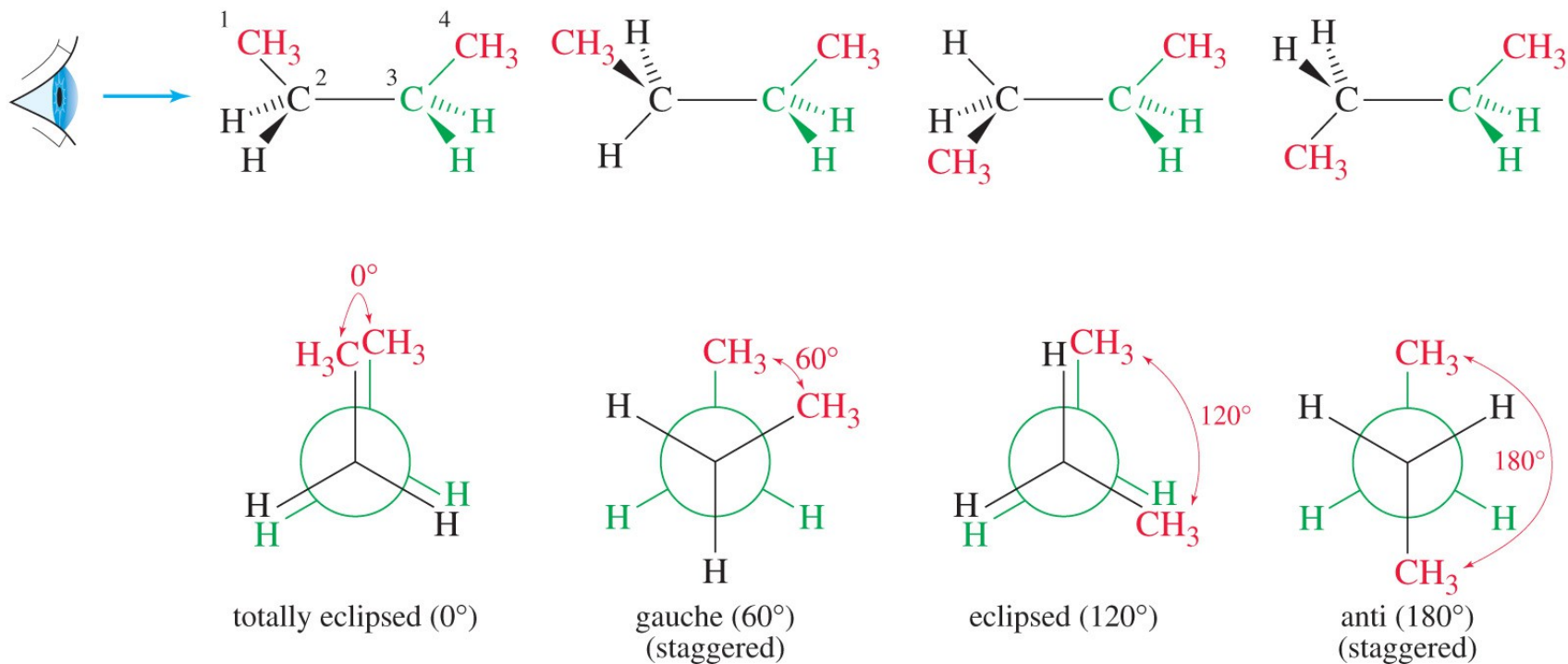
# Propane Conformations



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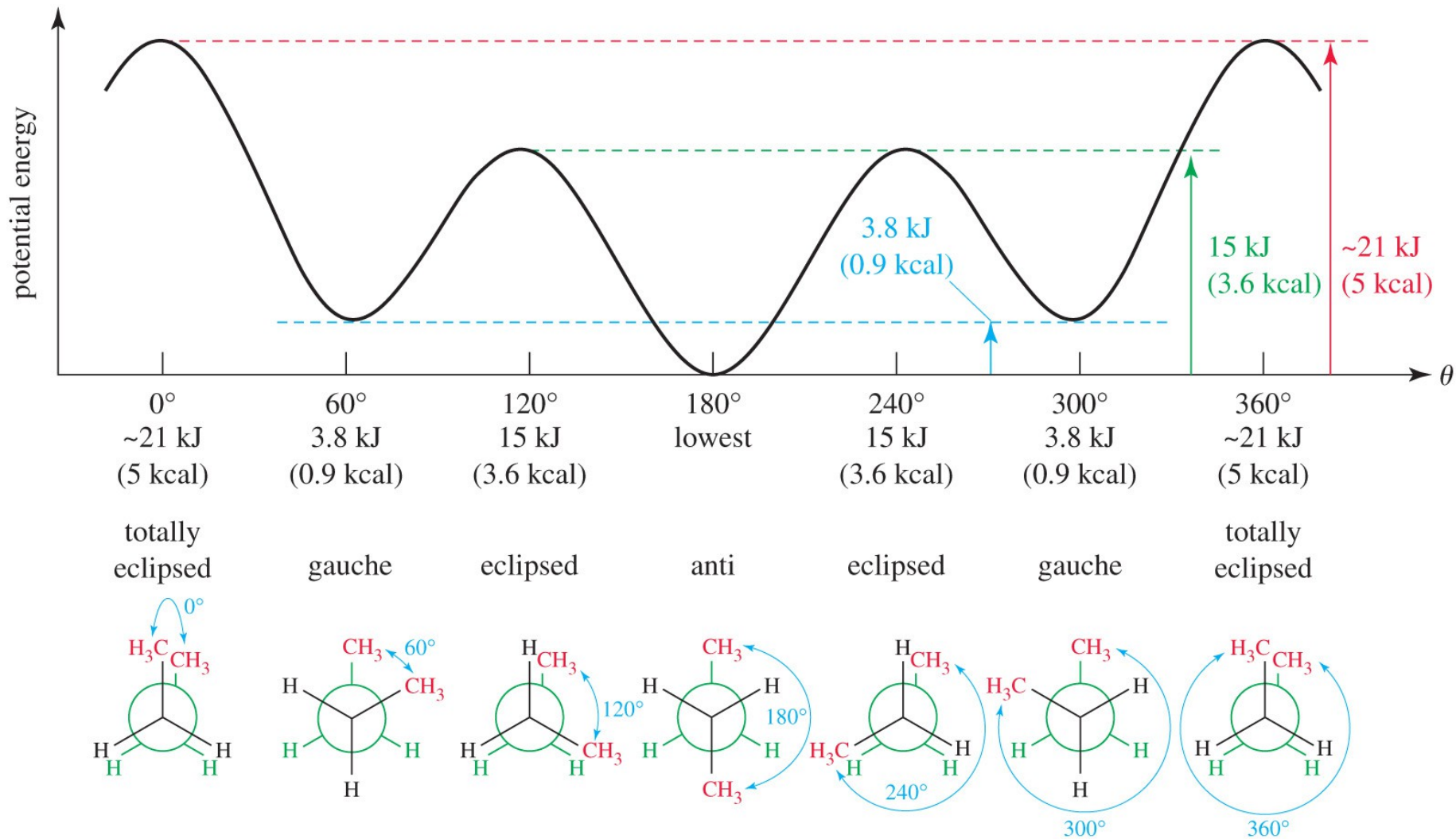
The staggered conformations of propane is lower in energy than the eclipsed conformations. Since the methyl group occupies more space than a hydrogen, the torsional strain will be 0.3 kcal/mol higher for propane than for ethane.

# Butane Conformations



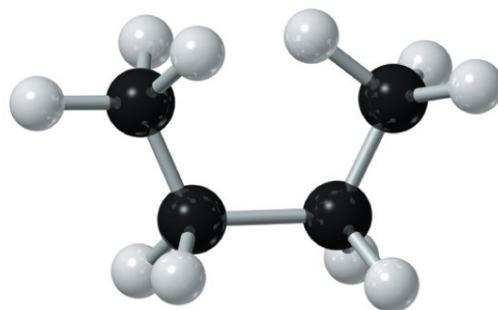
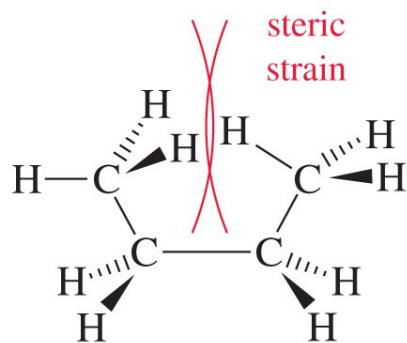
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- Butane has two different staggered conformations: gauche ( $60^\circ$  between the methyl groups) and anti ( $180^\circ$  between the methyl groups).
- The eclipsed conformation where the dihedral angle between the methyl groups is  $0^\circ$  is referred to as *totally eclipsed*.



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# Steric Strain

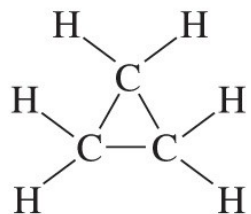


Totally eclipsed conformation of butane

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- The totally eclipsed conformation is higher in energy because it forces the two end methyl groups so close together that their electron clouds experience a strong repulsion.
- This kind of interference between two bulky groups is called *steric strain* or *steric hindrance*.

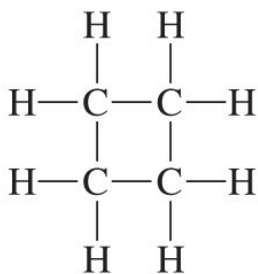
# Cycloalkanes: $C_nH_{2n}$



or



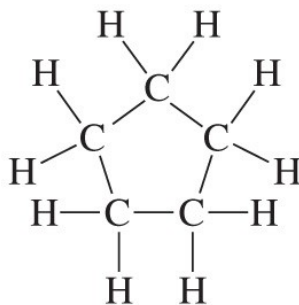
cyclopropane  
 $C_3H_6$



or



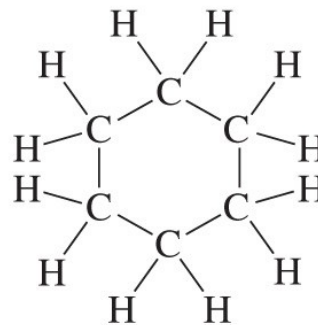
cyclobutane  
 $C_4H_8$



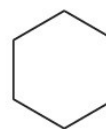
or



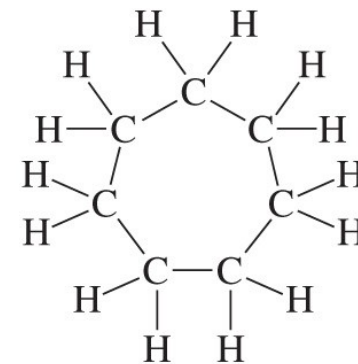
cyclopentane  
 $C_5H_{10}$



or



cyclohexane  
 $C_6H_{12}$



or



cycloheptane  
 $C_7H_{14}$

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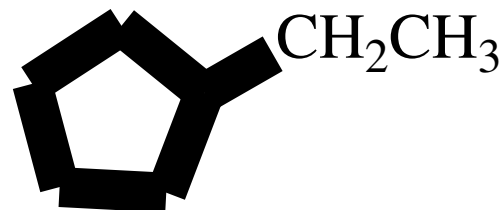


# Physical Properties

- Non-polar
- Relatively inert
- Boiling point and melting point depends on the molecular weight.

# Cycloalkane Nomenclature

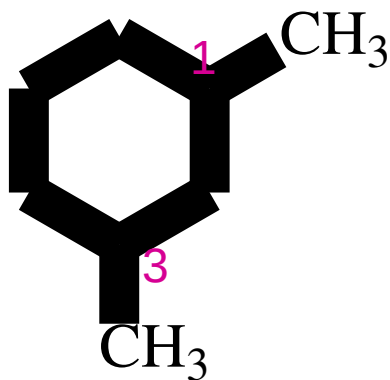
- Cycloalkane is the main chain: alkyl groups attached to the cycloalkane will be named as alkyl groups.
- If only one alkyl group is present, then no number is necessary.



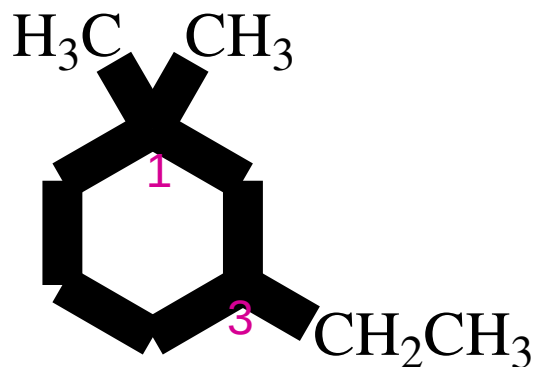
ethylcyclopentane

# Cycloalkane Nomenclature

- If there are two or more substituents, number the main chain to give all substituents the lowest possible number.

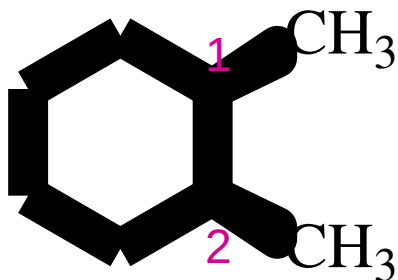


1,3-dimethylcyclohexane



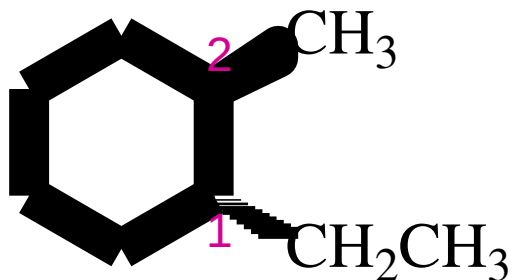
3-ethyl-1,1-dimethylcyclohexane

# Geometric Isomers



**Same side: *cis*-**

*cis*-1,2-dimethylcyclohexane



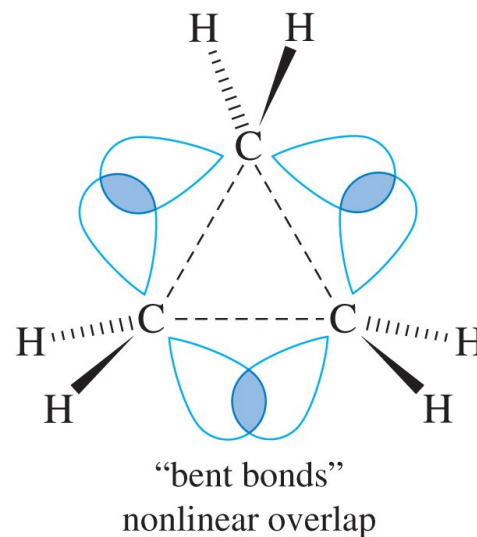
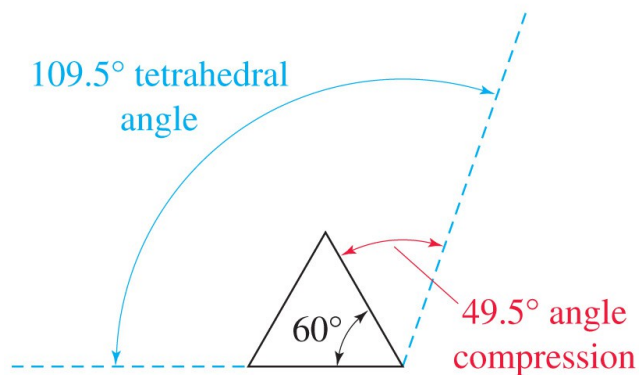
**Opposite side: *trans*-**

*trans*-1-ethyl-2-methylcyclohexane

# Stabilities of Cycloalkanes

- Five- and six-membered rings are the most common in nature.
- Carbons of cycloalkanes are  $sp^3$  hybridized and thus require an angle of  $109.5^\circ$ .
- When a cycloalkane has an angle other than  $109.5^\circ$ , there will not be optimum overlap and the compound will have *angle strain*.
- Angle strain is sometimes called *Baeyer strain* in honor of Adolf von Baeyer who first explained this phenomenon.
- *Torsional strain* arises when all the bonds are eclipsed.

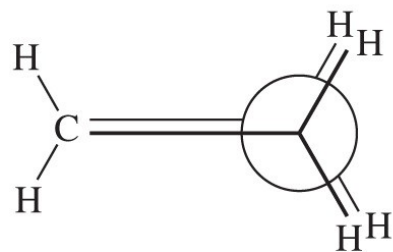
# Cyclopropane: $C_3H_6$



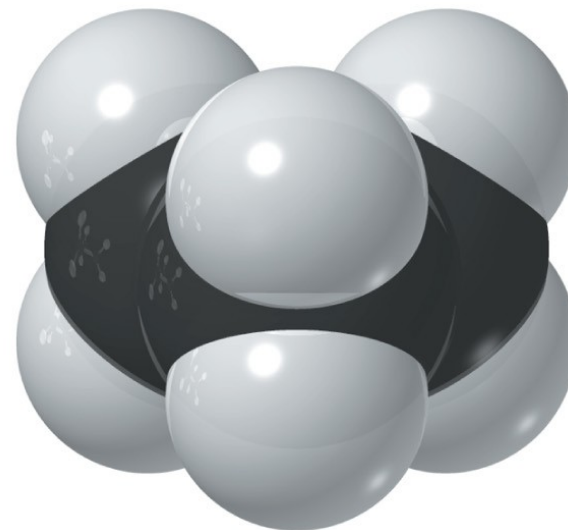
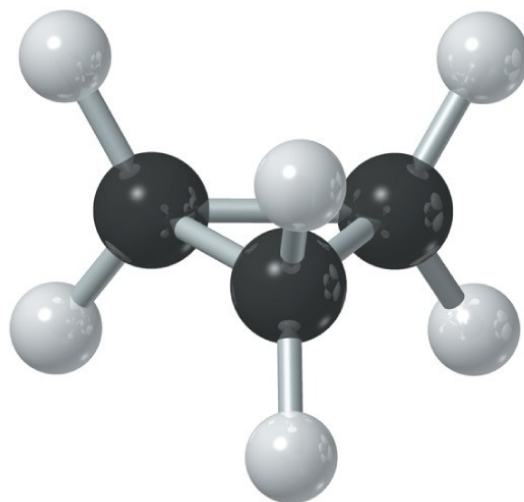
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- The bond angles are compressed to  $60^\circ$  from the usual  $109.5^\circ$  bond angle of  $sp^3$  hybridized carbon atoms.
- This severe angle strain leads to nonlinear overlap of the  $sp^3$  orbitals and “bent bonds”.

# Torsional Strain



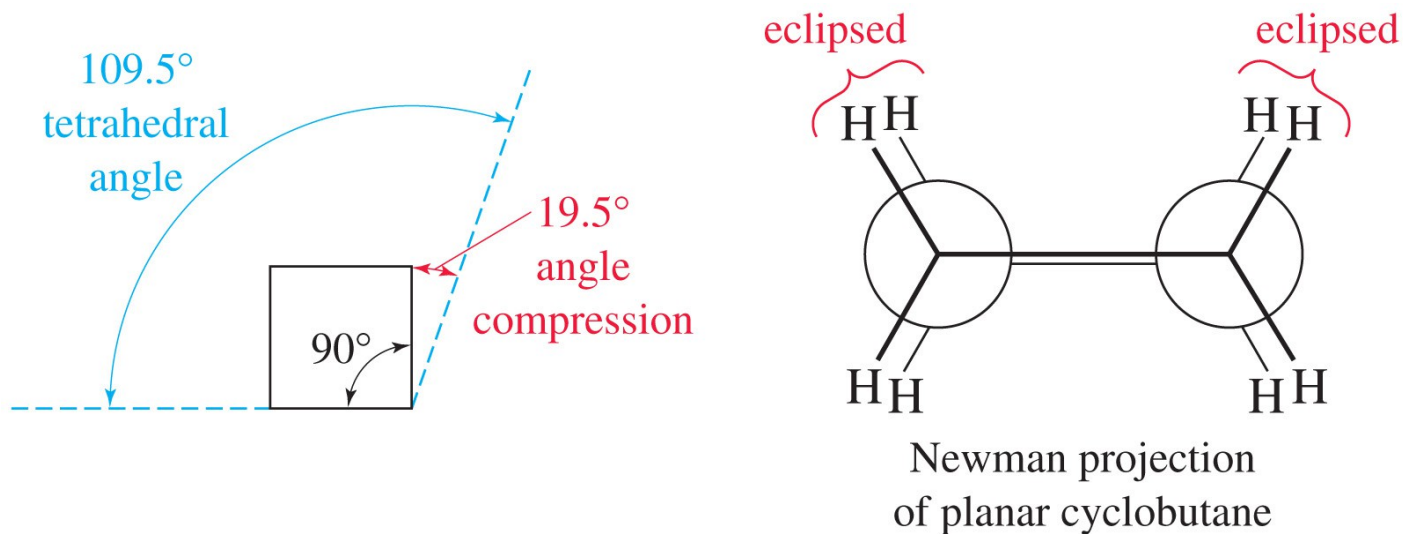
Newman projection  
of cyclopropane



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All the C—C bonds are eclipsed, generating torsional strain that contributes to the total ring strain.

# Cyclobutane: C<sub>4</sub>H<sub>8</sub>

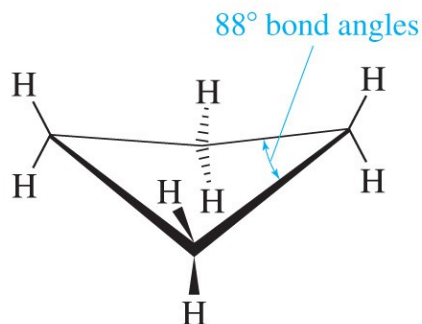


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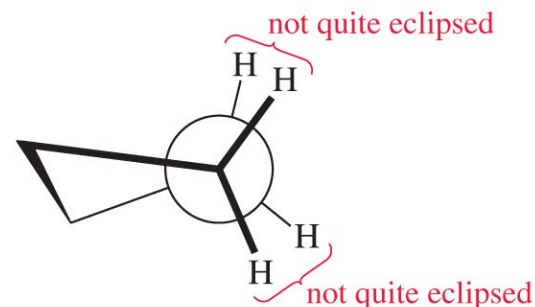
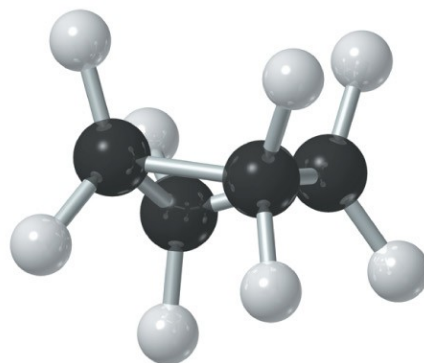
The ring strain of a planar cyclobutane results from two factors: **angle strain** from the compressing of the bond angles to 90° rather than the tetrahedral angle of 109.5° and **torsional strain** from eclipsing of the bonds.



# Non-Planar Cyclobutane



slightly folded conformation

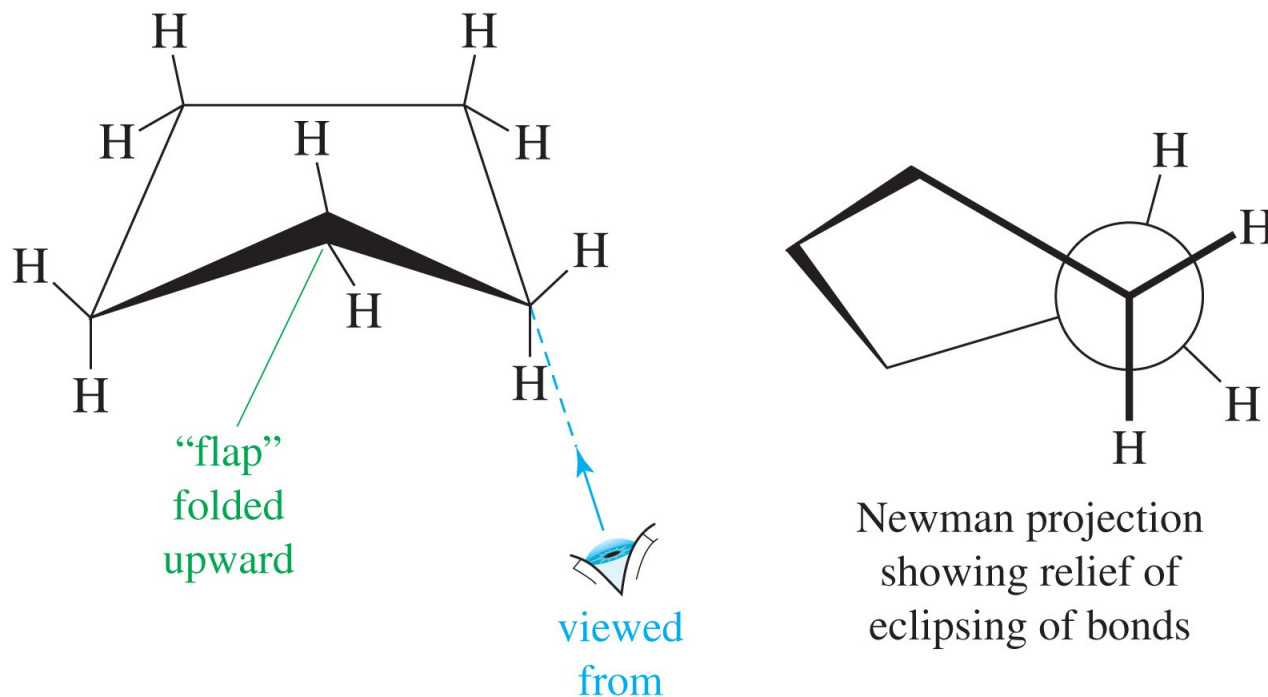


Newman projection of one bond

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- Cyclic compound with four carbons or more adopt non-planar conformations to relieve ring strain.
- Cyclobutane adopts the folded conformation (“envelope”) to decrease the torsional strain caused by eclipsing hydrogens.

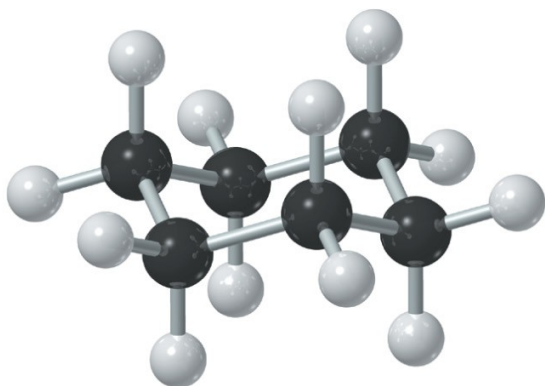
# Cyclopentane: C<sub>5</sub>H<sub>10</sub>



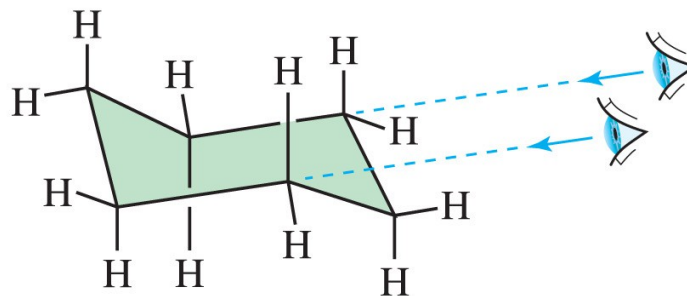
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The conformation of cyclopentane is slightly folded, like the shape of an envelope. This puckered conformation reduces the eclipsing of adjacent methylene (CH<sub>2</sub>) groups.

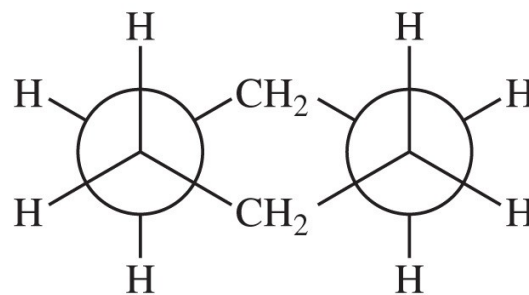
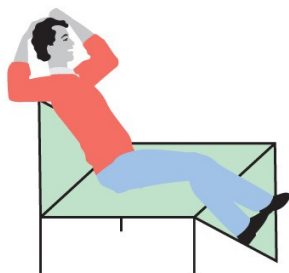
# Chair Conformation of Cyclohexane



chair conformation



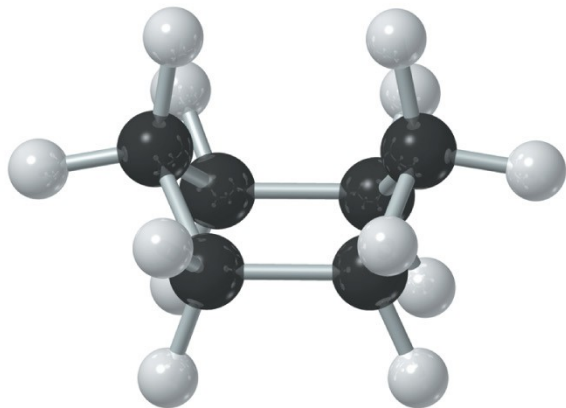
viewed along the "seat" bonds



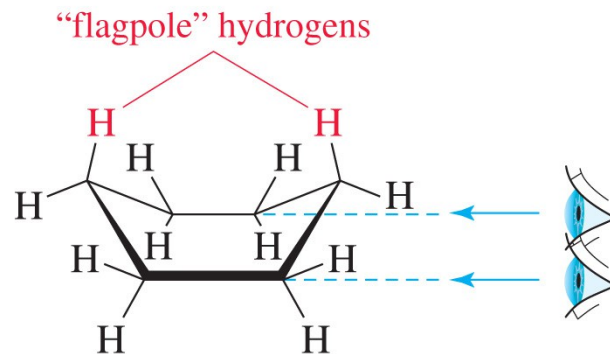
Newman projection

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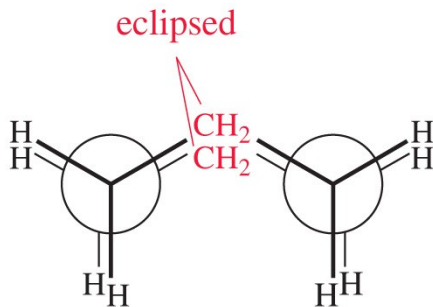
# Boat Conformation of Cyclohexane



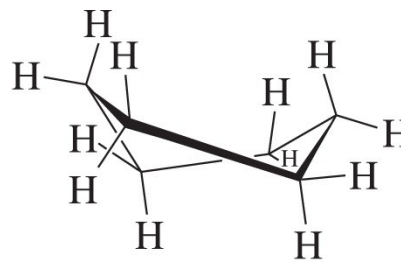
boat conformation



symmetrical boat



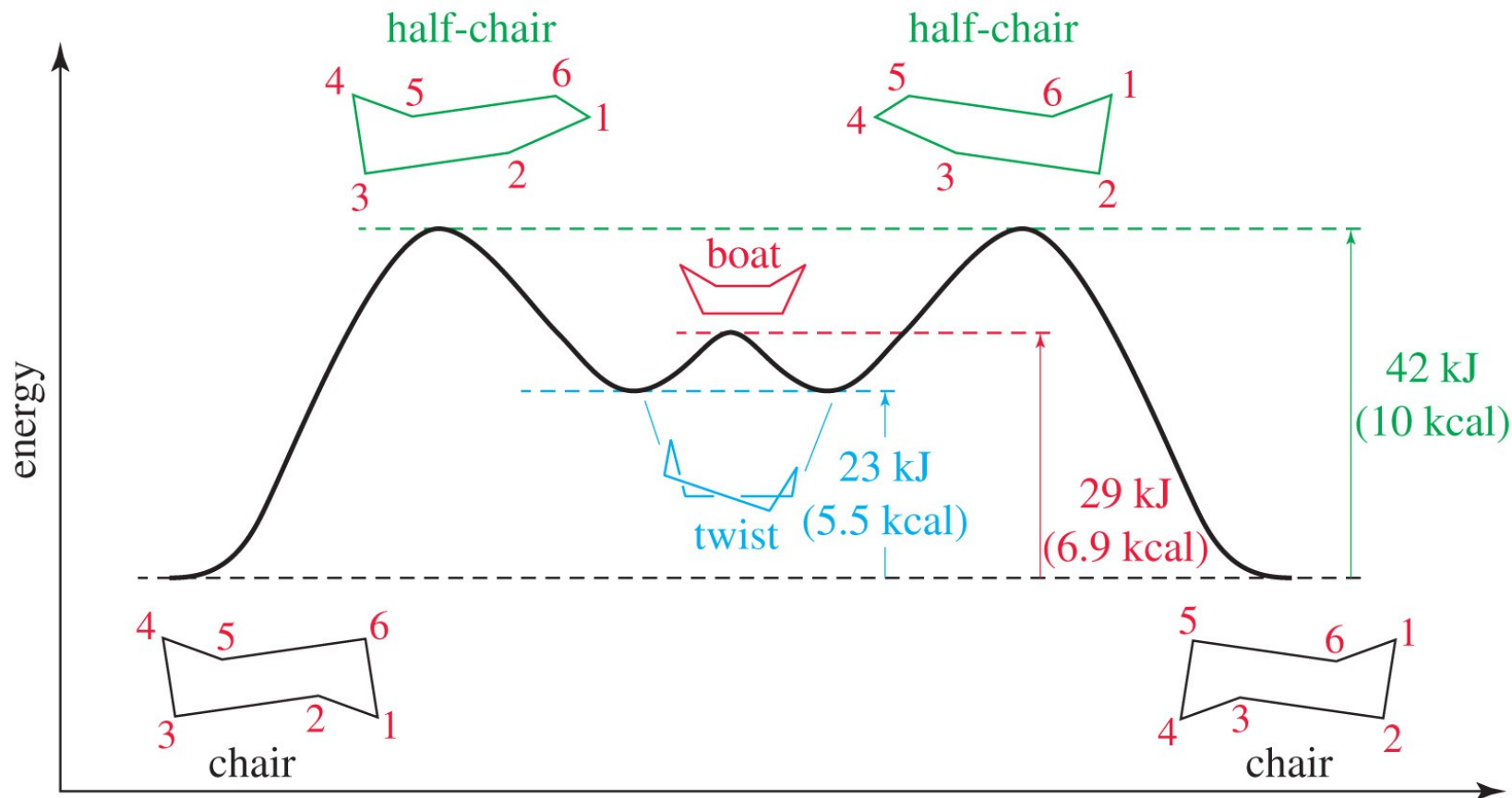
Newman projection



"twist" boat

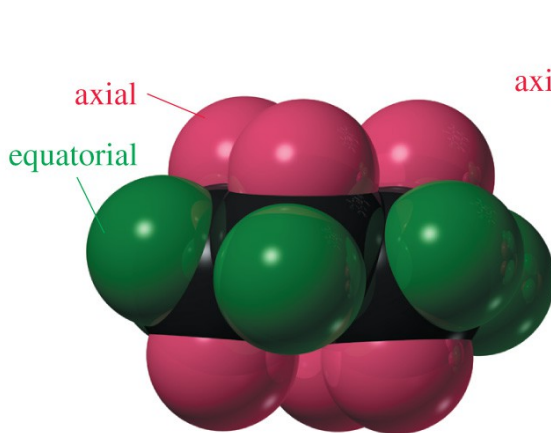
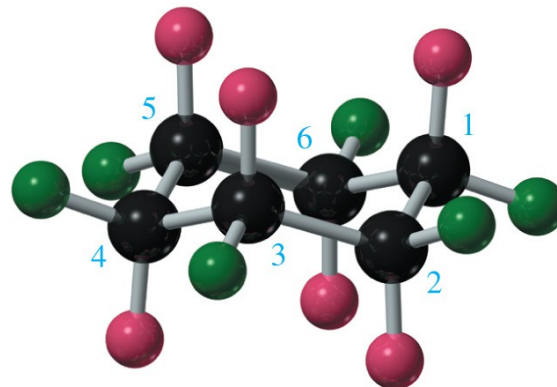
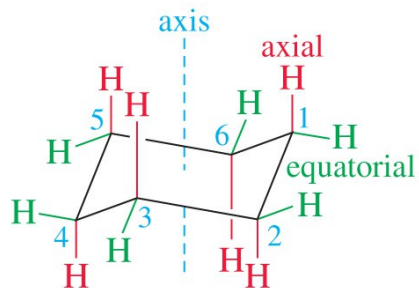
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# Conformational Energy Diagram of Cyclohexane

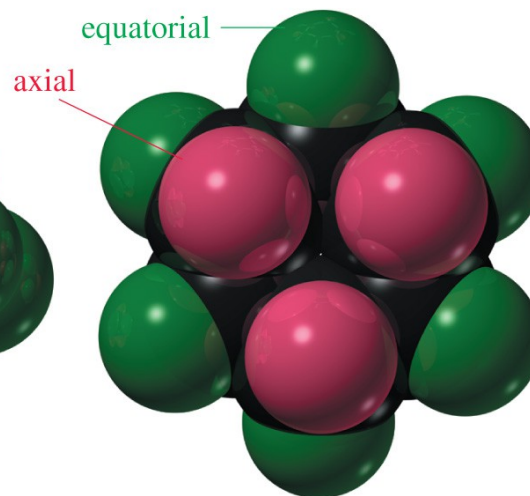


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# Axial and Equatorial Positions



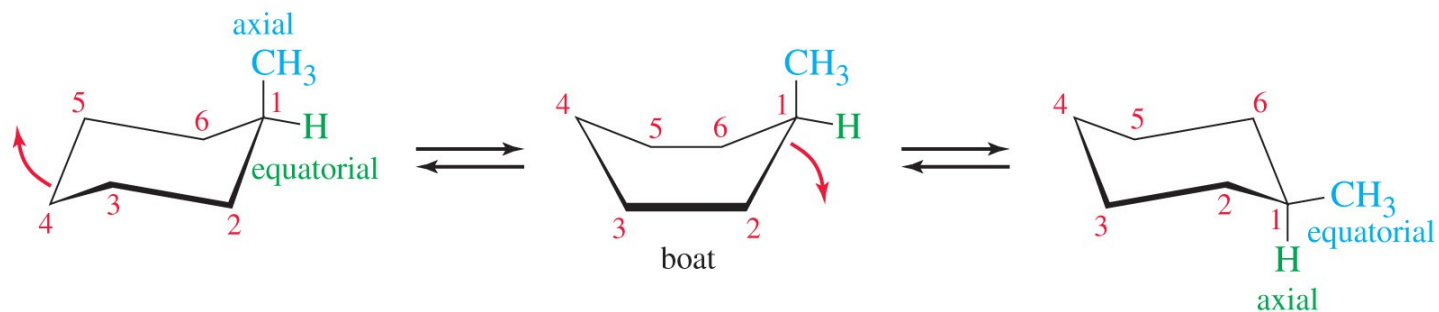
seen from the side



seen from above

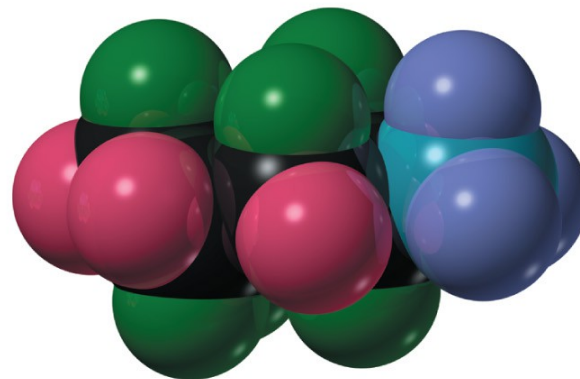
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# Chair–Chair Interconversion



$\text{CH}_3$  axial

ring-flip

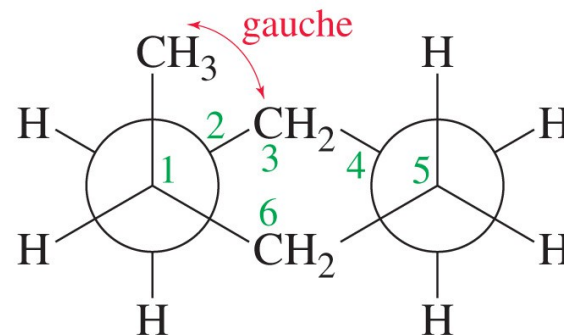
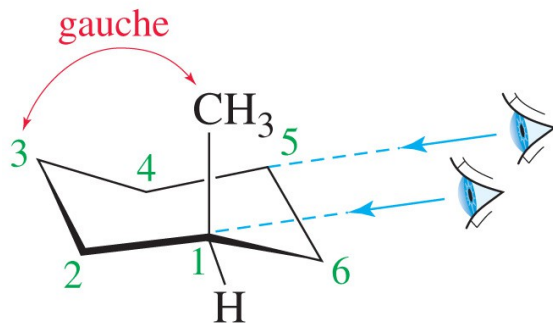


$\text{CH}_3$  equatorial

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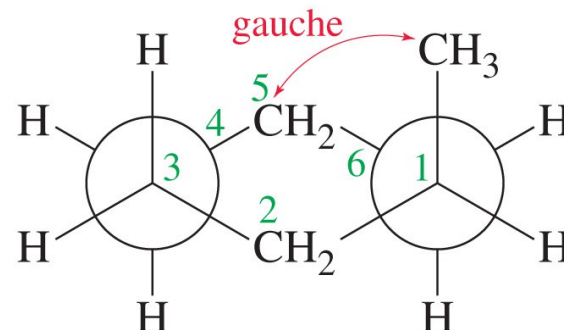
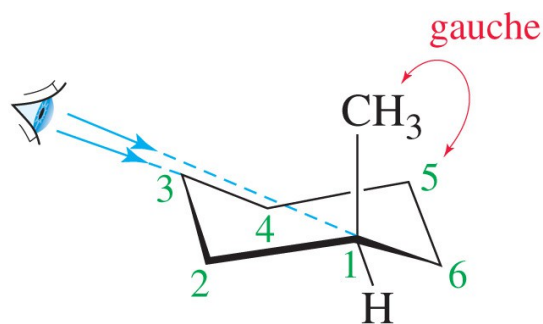
The most important result in chair conversion is that any substituent that is **axial** in the original conformation becomes **equatorial** in the new conformation.

# Axial Methyl in Methylcyclohexane



Newman projection

(a)

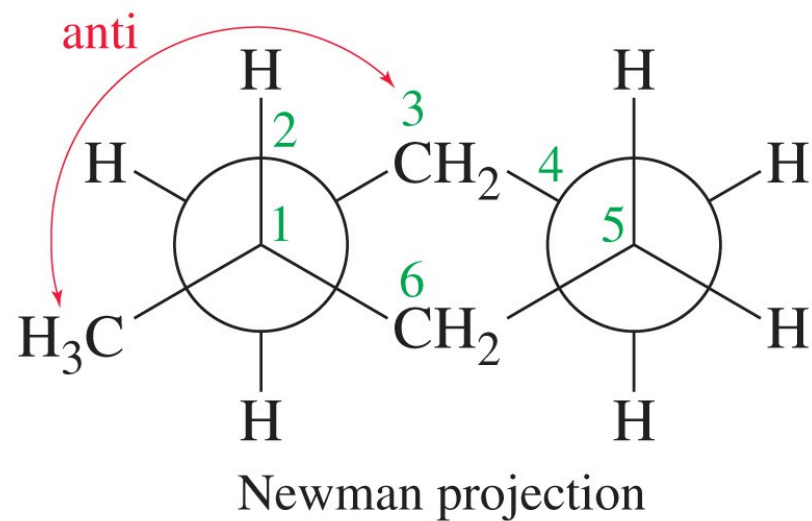
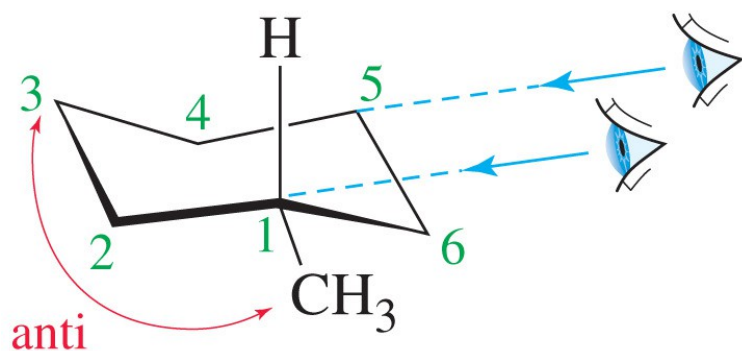


Newman projection

(b)

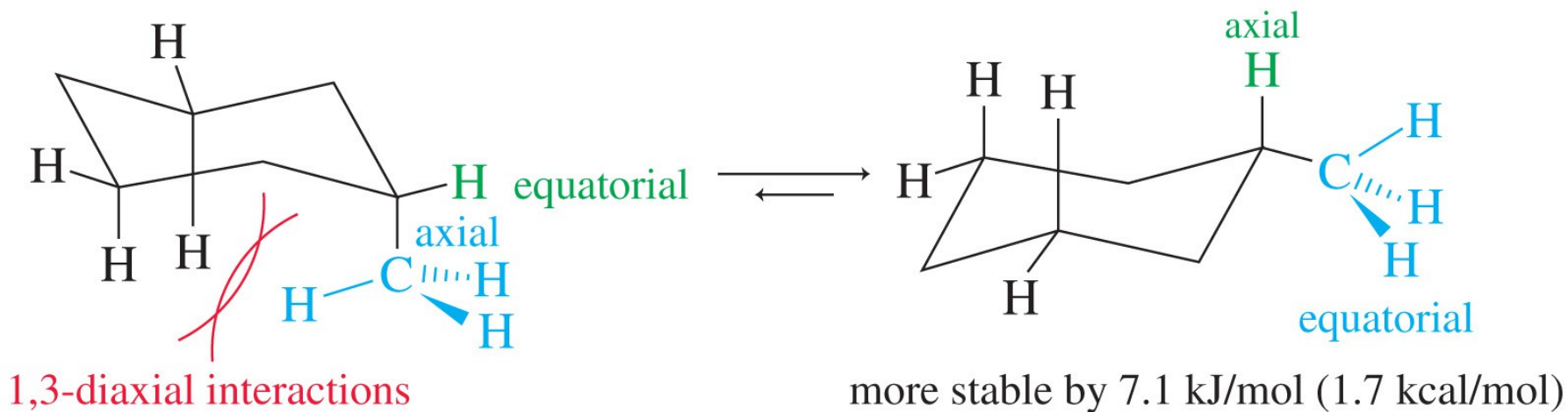


# Equatorial Methyl Group



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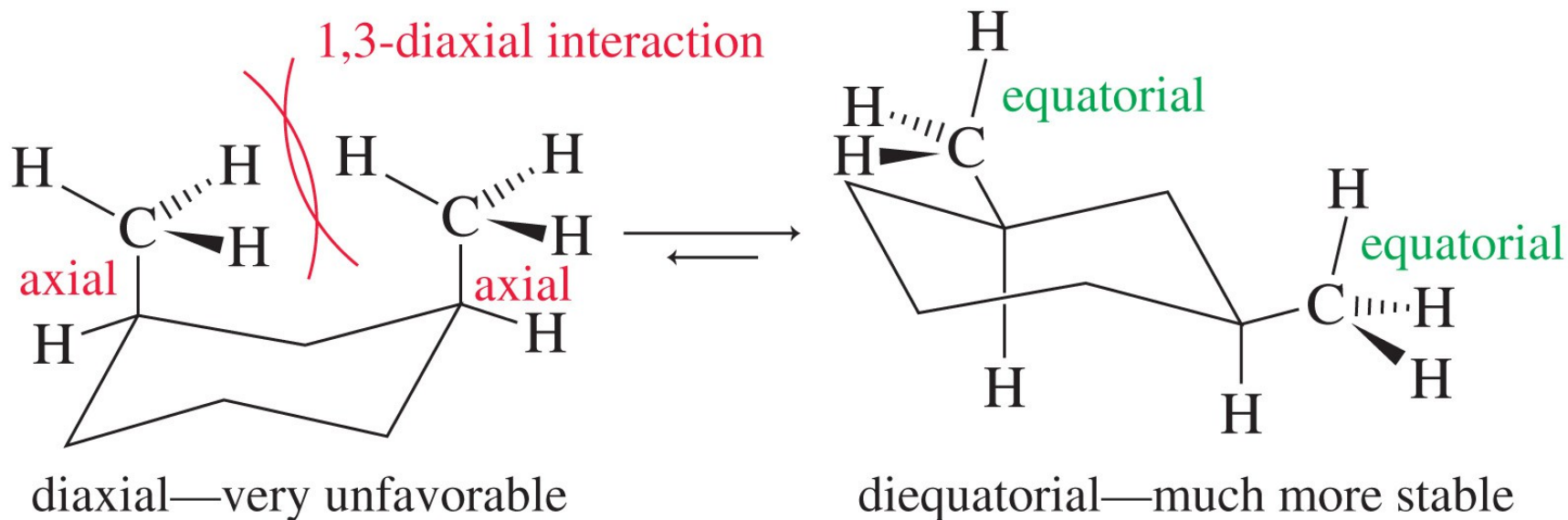
# 1,3-Diaxial Interaction



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The axial substituent interferes with the axial hydrogens on C3 and C5. This interference is called a *1,3-diaxial interaction*.

# Cis-1,3-dimethylcyclohexane

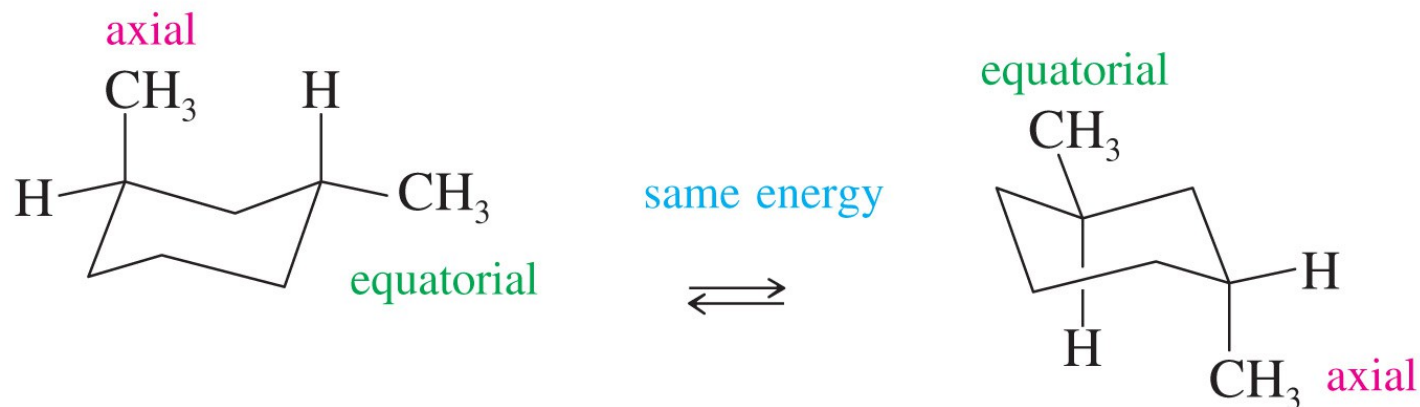


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- *Cis*-1,3-dimethylcyclohexane can have both methyl groups in axial positions or both in equatorial positions.
- The conformation with both methyl groups being equatorial is more stable.

# Trans-1,3-dimethylcyclohexane

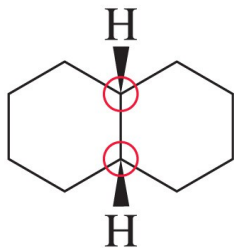
*Chair conformations of trans-1,3-dimethylcyclohexane*



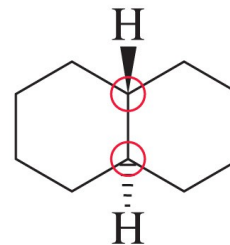
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Both conformations have one axial and one equatorial methyl group so they have the same energy.

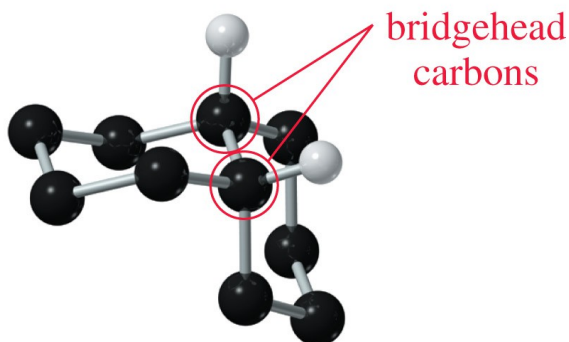
# Decalin



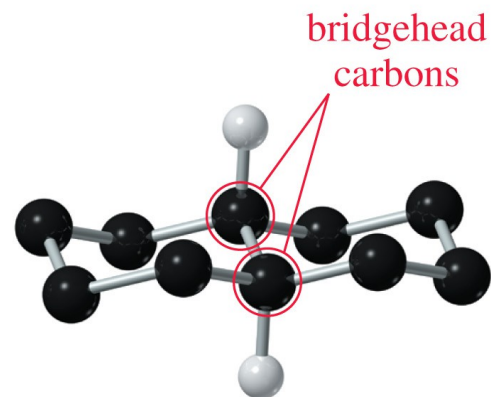
*cis*-decalin



*trans*-decalin



*cis*-decalin

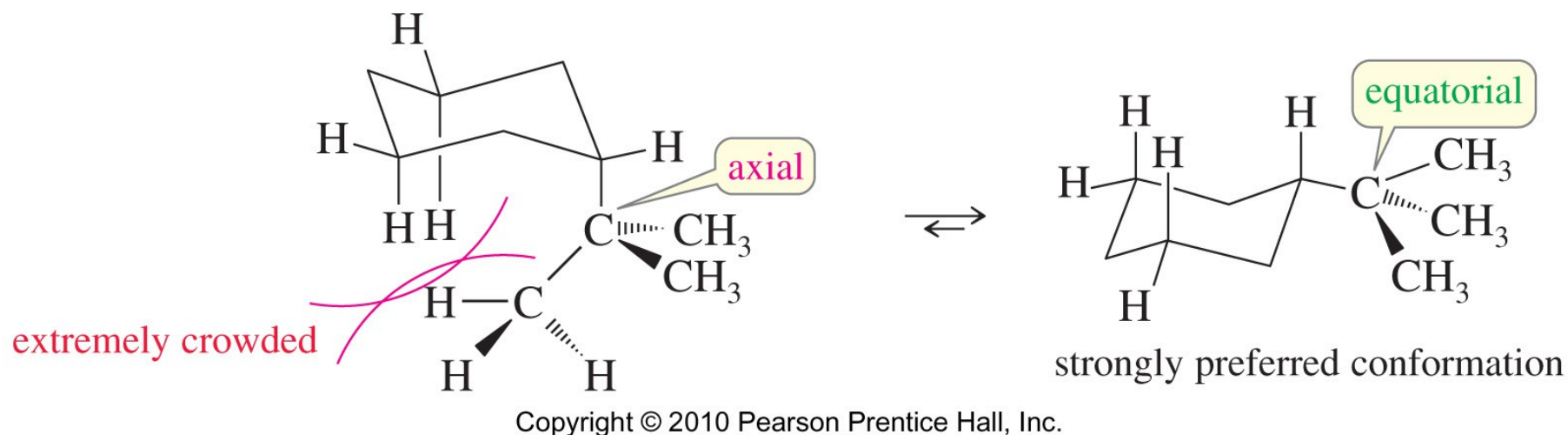


*trans*-decalin

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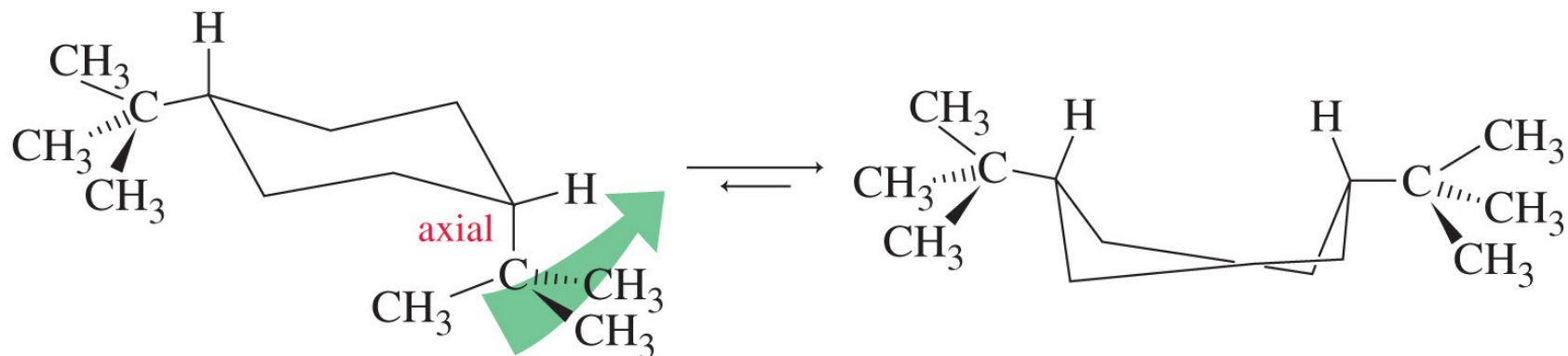
*Cis*-decalin has a ring fusion where the second ring is attached by two *cis* bonds. *Trans*-decalin is fused using two *trans* bonds. *Trans*-decalin is more stable because the alkyl groups are equatorial.

# *Tert*-butylcyclohexane



Substituents are less crowded in the equatorial positions.

# Cis-1,4-ditertbutylcyclohexane



*tert*-butyl group moves out of the axial position

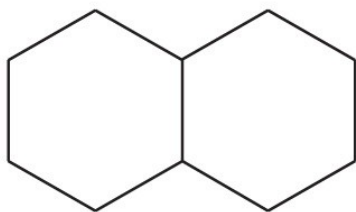
twist boat

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The most stable conformation of *cis*-1,4-di-*tert*butylcyclohexane is the twist boat. Both chair conformations require one of the bulky *t*-butyl groups to occupy an axial position.

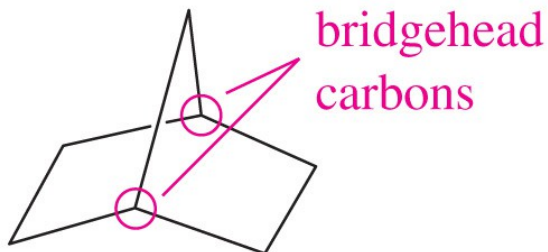
# Bicyclic Systems

*fused bicyclic*



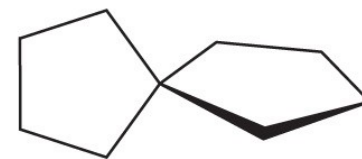
bicyclo[4.4.0]decane  
(decalin)

*bridged bicyclic*



bicyclo[2.2.1]heptane  
(norbornane)

*spirocyclic*

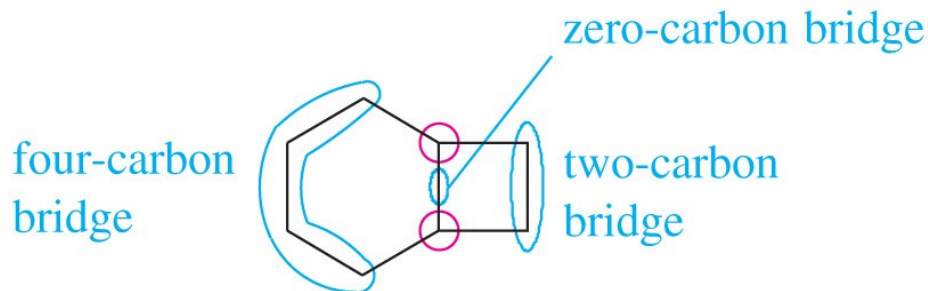


spiro[4.4]nonane

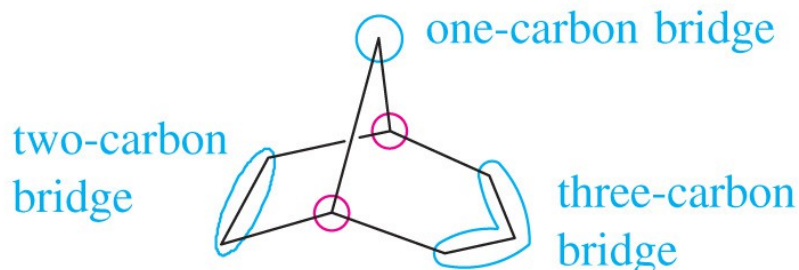
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# Nomenclature of Bicyclic Systems



bicyclo[4.2.0]octane



bicyclo[3.2.1]octane

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## Bicyclo [#.#.#]alkane

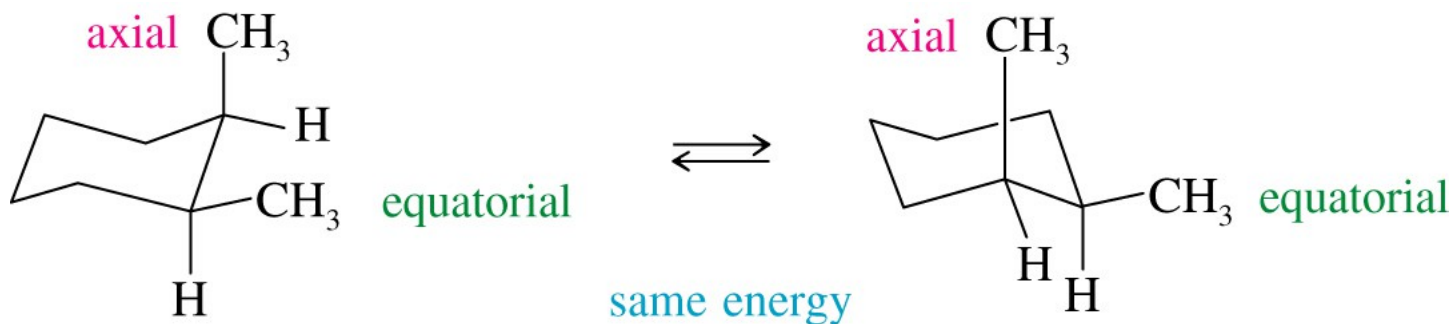
Where # are the number of carbons on the bridges (in decreasing order) and the alkane name includes all the carbons in the compound.

## Solved Problem 3-3

- (a) Draw both chair conformations of *cis*-1,2-dimethylcyclohexane, and determine which conformer is more stable.
- (b) Repeat for the *trans* isomer.
- (c) Predict which isomer (*cis* or *trans*) is more stable.

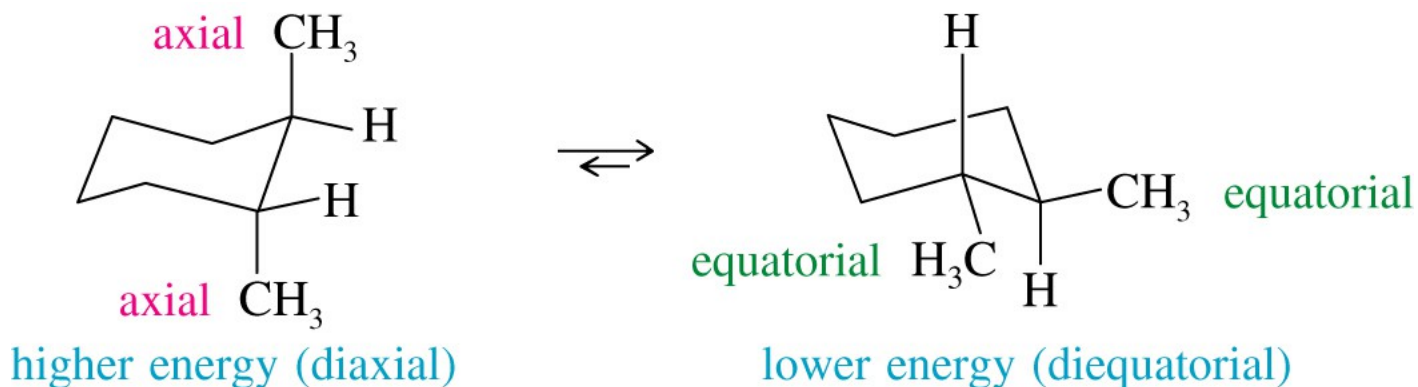
# Solved Problem 3-3: Solution (a)

a) There are two possible chair conformations for the cis isomer, and these two conformations interconvert at room temperature. Each of these conformations places one methyl group axial and one equatorial, giving them the same energy.



# Solved Problem 3-3 : Solution (b)

(b) There are two chair conformations of the trans isomer that interconvert at room temperature. Both methyl groups are axial in one, and both are equatorial in the other. The diequatorial conformation is more stable because neither methyl group occupies the more hindered axial position.



## Solved Problem 3-3 : Solution (c)

(c) The trans isomer is more stable. The most stable conformation of the trans isomer is diequatorial and therefore about 7.6 kJ/mol (1.8 kcal/mol) lower in energy than either conformation of the cis isomer, each having one methyl axial and one equatorial. Remember that cis and trans are distinct isomers and cannot interconvert.

# Solved Problem 3-1

Draw the most stable conformation of *trans*-1-ethyl-3-methylcyclohexane.

Solution: First, we draw the two conformations. The ethyl group is bulkier than the methyl group, so the conformation with the ethyl group equatorial is more stable.

