Organic Chemistry

Second Edition

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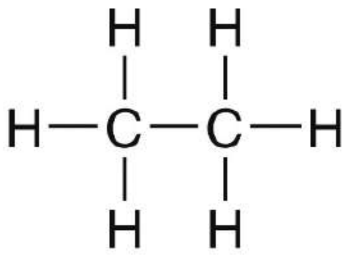
Chapter 4

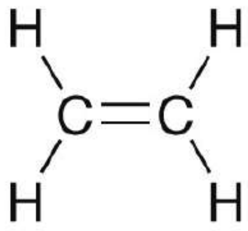
Alkanes and Cycloalkanes

4.1 Alkanes

- Hydrocarbons – compounds that are only composed of hydrogen and carbon



Ethane
C_2H_6



Ethylene
C_2H_4

Acetylene
C_2H_2

Benzene
C_6H_6

- Which of the molecules above is saturated with hydrogen atoms?

4.1 Alkanes

- Saturated Hydrocarbons do NOT contain any pi bonds

Propane

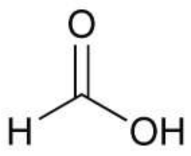
Butane

Pentane

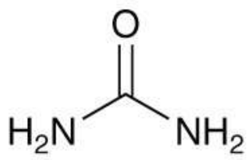
- When communicating about molecules, each unique molecule must have a unique name
- The suffix -ane is used for saturated hydrocarbons
- How are the above hydrocarbons different?

4.2 Naming Alkanes

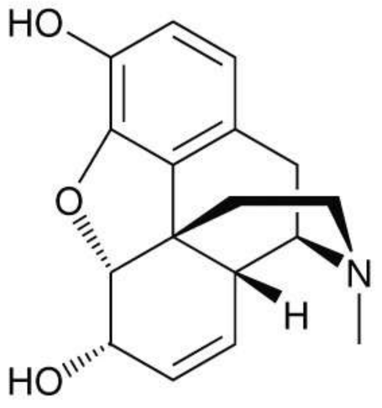
- Many organic compounds have common names



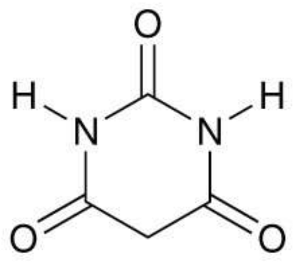
Formic acid
Isolated from ants
and named after the
Latin word for ant, *formica*



Urea
Isolated from urine



Morphine
A painkiller named after
the Greek God of dreams,
Morpheus



Barbituric acid
Adolf von Baeyer named this
compound in honor of a
woman named Barbara

- Some common names have been used for hundreds of years and are still frequently used.

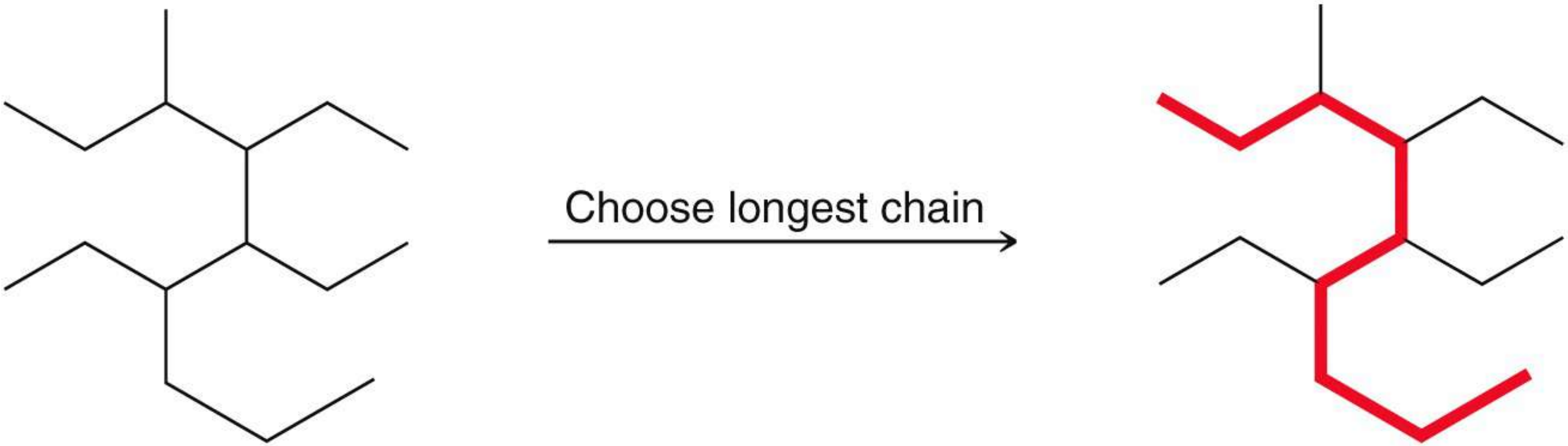
4.2 Naming Alkanes

- In 1892, as the number of known molecules grew, chemists decided that a SYSTEMATIC naming system was needed
- **IUPAC system** – International Union of Pure and Applied Chemistry
- We can learn the IUPAC system instead of having to memorize a common name for every molecule

4.2 Finding The Parent Chain

- The **IUPAC** system

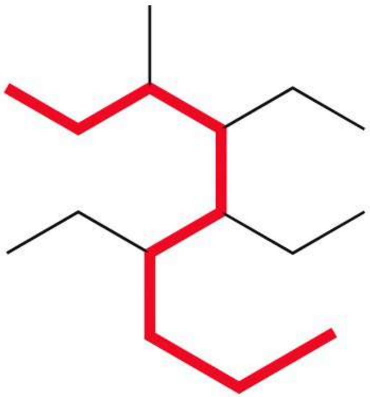
1. Find the parent chain - the longest consecutive chain of carbons



Parent has 9 carbon atoms

4.2 Finding The Parent Chain

1. Find the parent chain - the longest consecutive chain of carbons



Parent has 9 carbon atoms

  - Use table 4.1 to look up the prefix that corresponds with the number of carbons in the parent chain

4.2 Finding The Parent Chain

1. Find the parent chain – if the parent chain has 9 carbons, the parent name is nonane

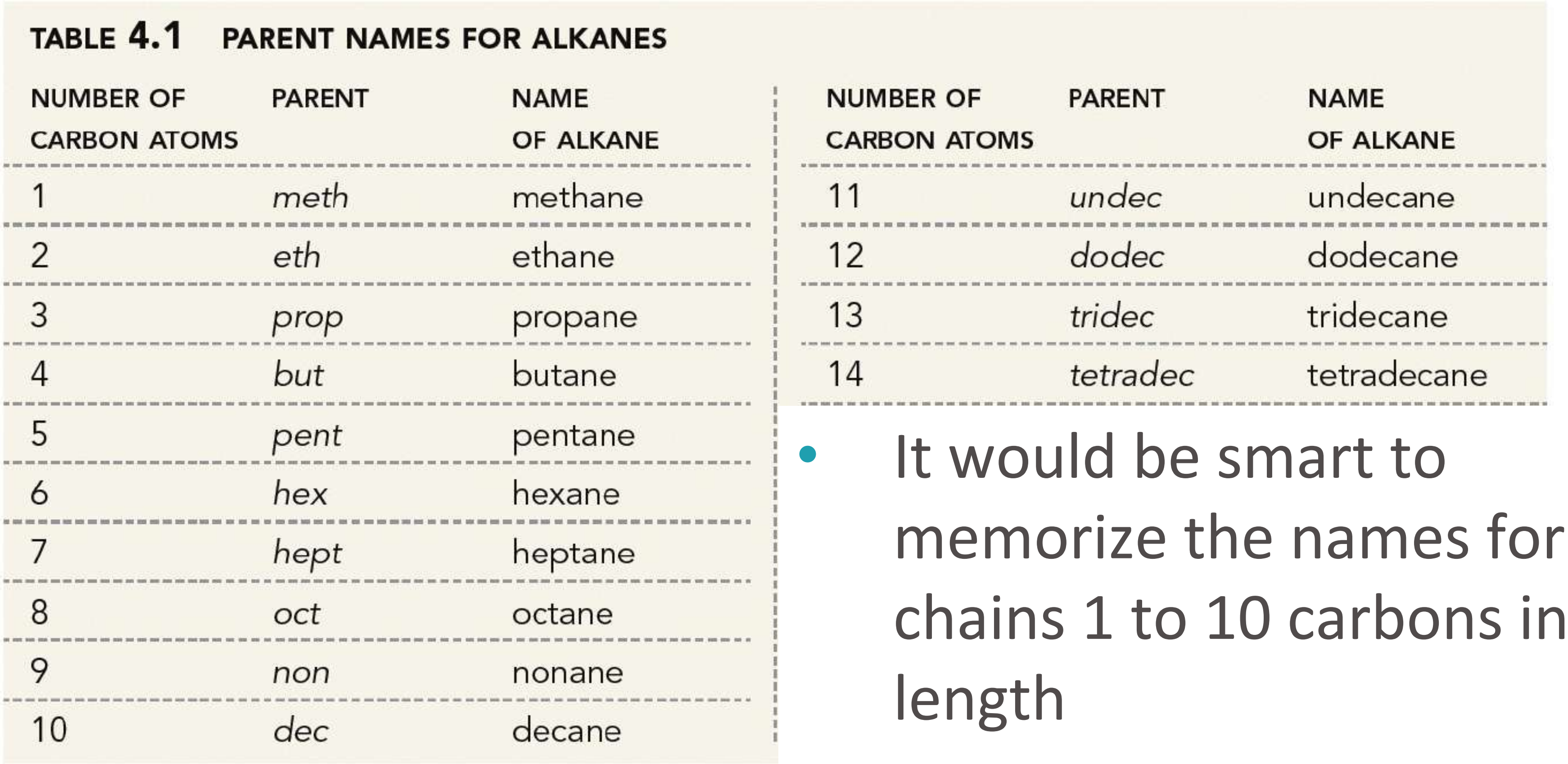


TABLE 4.1 PARENT NAMES FOR ALKANES

NUMBER OF CARBON ATOMS	PARENT	NAME OF ALKANE
1	*meth*	methane
2	*eth*	ethane
3	*prop*	propane
4	*but*	butane
5	*pent*	pentane
6	*hex*	hexane
7	*hept*	heptane
8	*oct*	octane
9	*non*	nonane
10	*dec*	decane
11	*undec*	undecane
12	*dodec*	dodecane
13	*tridec*	tridecane
14	*tetradec*	tetradecane

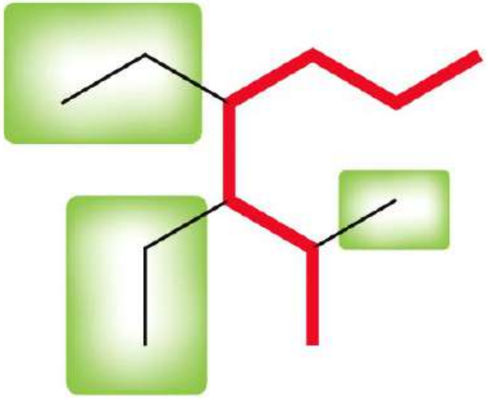
- It would be smart to memorize the names for chains 1 to 10 carbons in length

4.2 Finding The Parent Chain

1. Find the parent chain
   - If there is more than one possible parent chain, choose the one with the most substituents attached

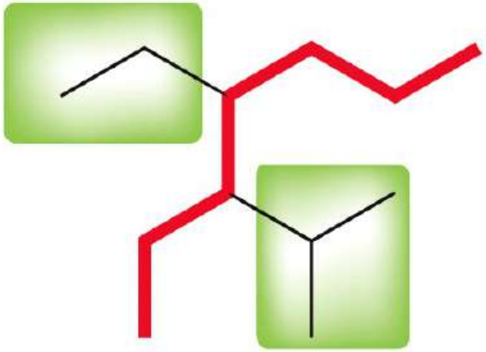
What is the parent name for this compound?

Correct
(3 substituents)



Parent has 7 carbon atoms

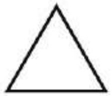
Incorrect
(2 substituents)



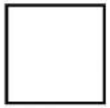
Parent has 7 carbon atoms

4.2 Finding The Parent Chain

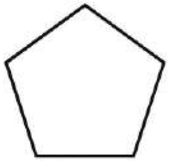
1. Find the parent chain
   - If the parent chain is cyclic (a ring of carbons), add the prefix, “cyclo” to the beginning of the parent name



Cyclopropane



Cyclobutane

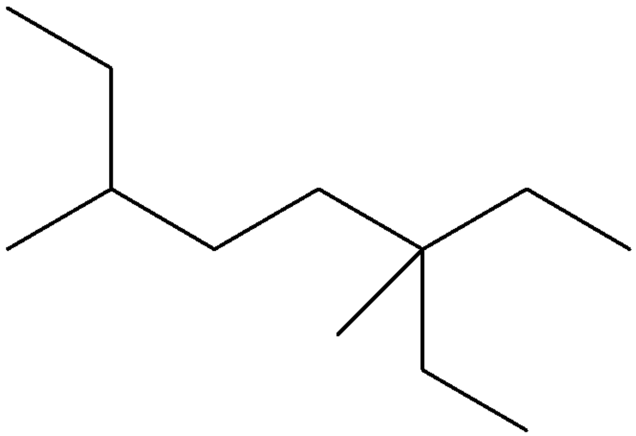


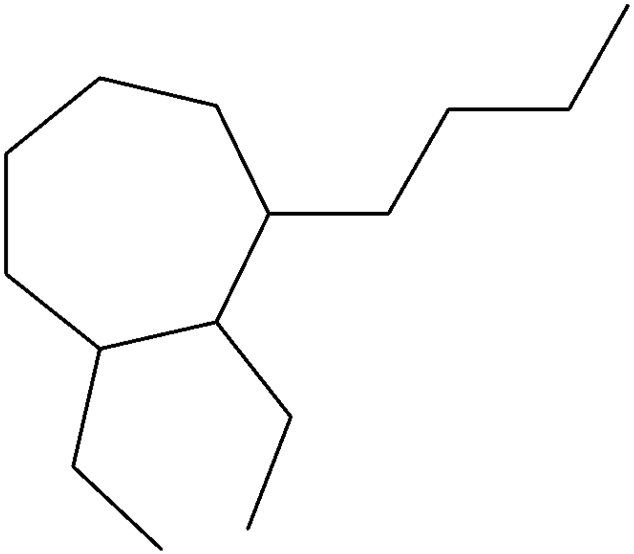
Cyclopentane

- Practice with SkillBuilder 4.1

4.2 Finding The Parent Chain

1. Find the parent chain
   - Give the parent name for the following compounds

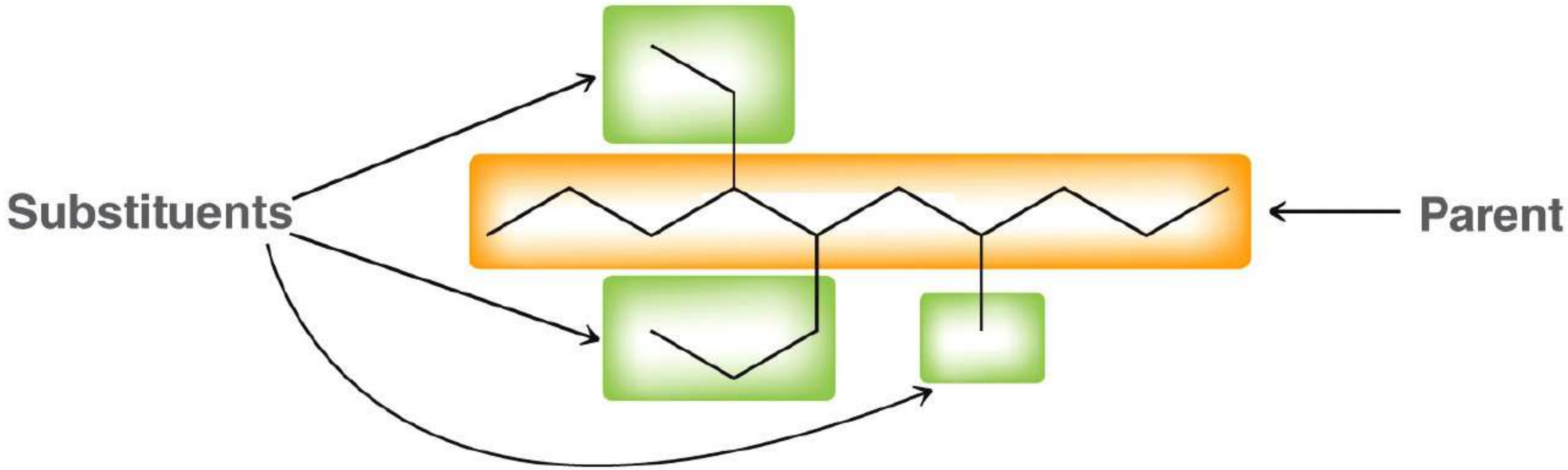




   - The parent name may NOT include carbons that are both in a ring and outside a ring.

4.2 Identifying Substituents

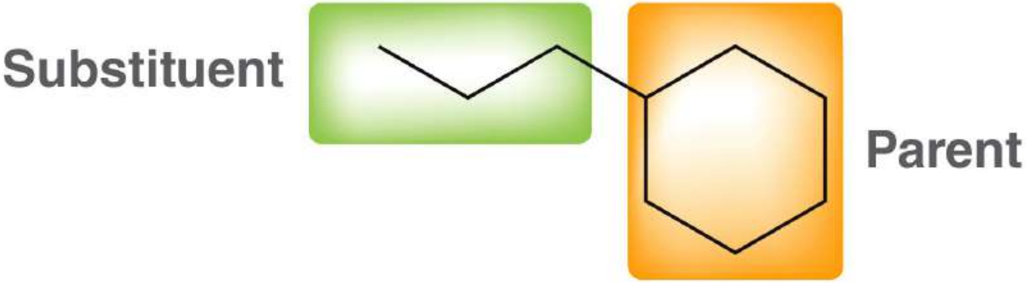
2. Identify substituents



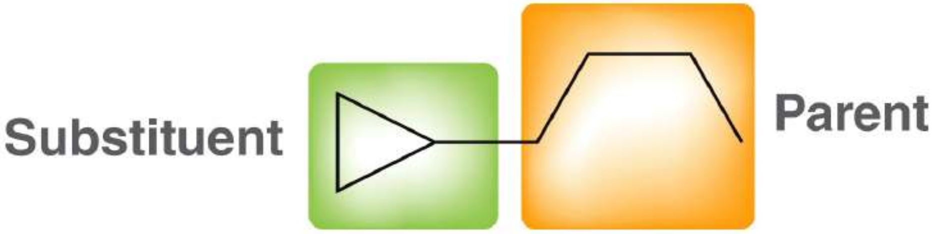
- Count the number of carbons in each side group, and use the terms from Table 4.2 to name the substituents
- The terms in Table 4.2 are the same as those in Table 4.1, except they end in yl instead of ane.
- Name the parent and substituents above

4.2 Identifying Substituents

2. Identify substituents (side groups)
   - A ring can be either a parent chain or a substituent depending on the number of carbons



Propylcyclohexane

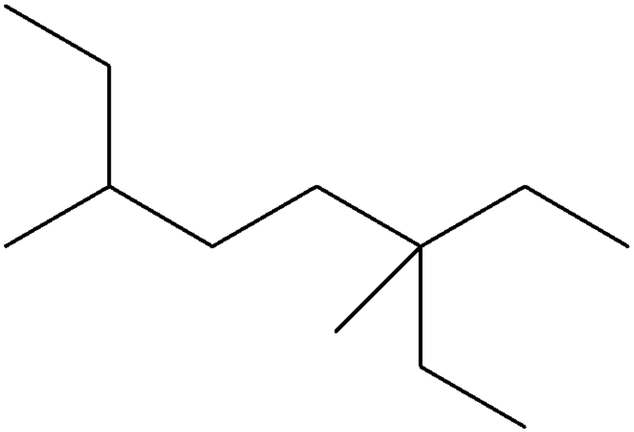


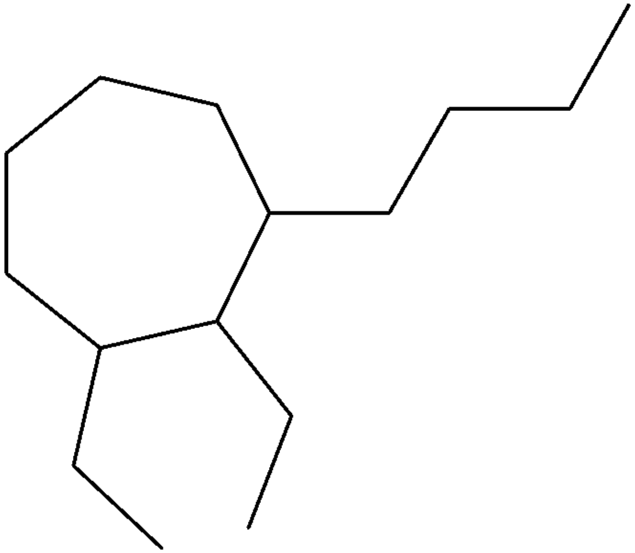
1-Cyclopropylbutane

- Practice with SkillBuilder 4

4.2 Identifying Substituents

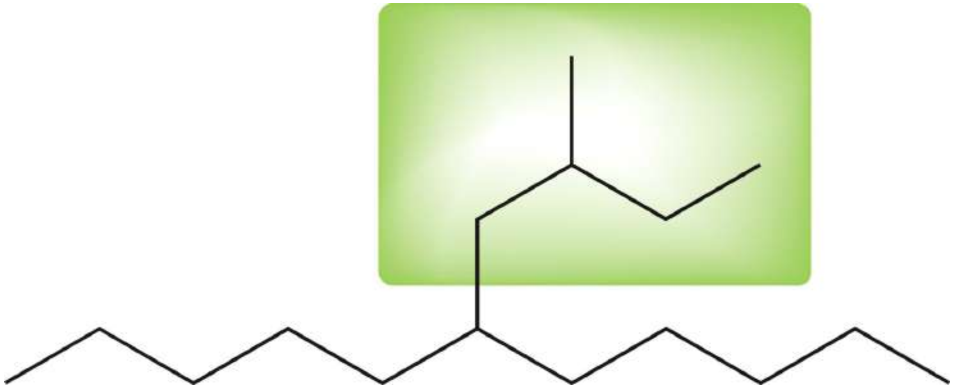
2. Identify substituents (side groups)
   - Name the substituents in the following molecules





4.2 Identifying Substituents

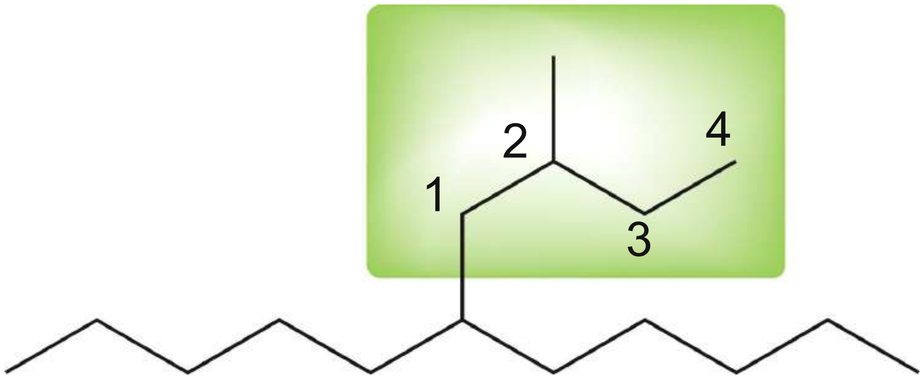
2. Identify substituents (side groups)
   - Some substituents have complex branches



   - How many carbons are in the highlighted substituent above?
   - Why is it improper to name it a PENTYL group?

4.2 Identifying Substituents

2. Identify substituents (side groups)
   - For substituents with complex branches

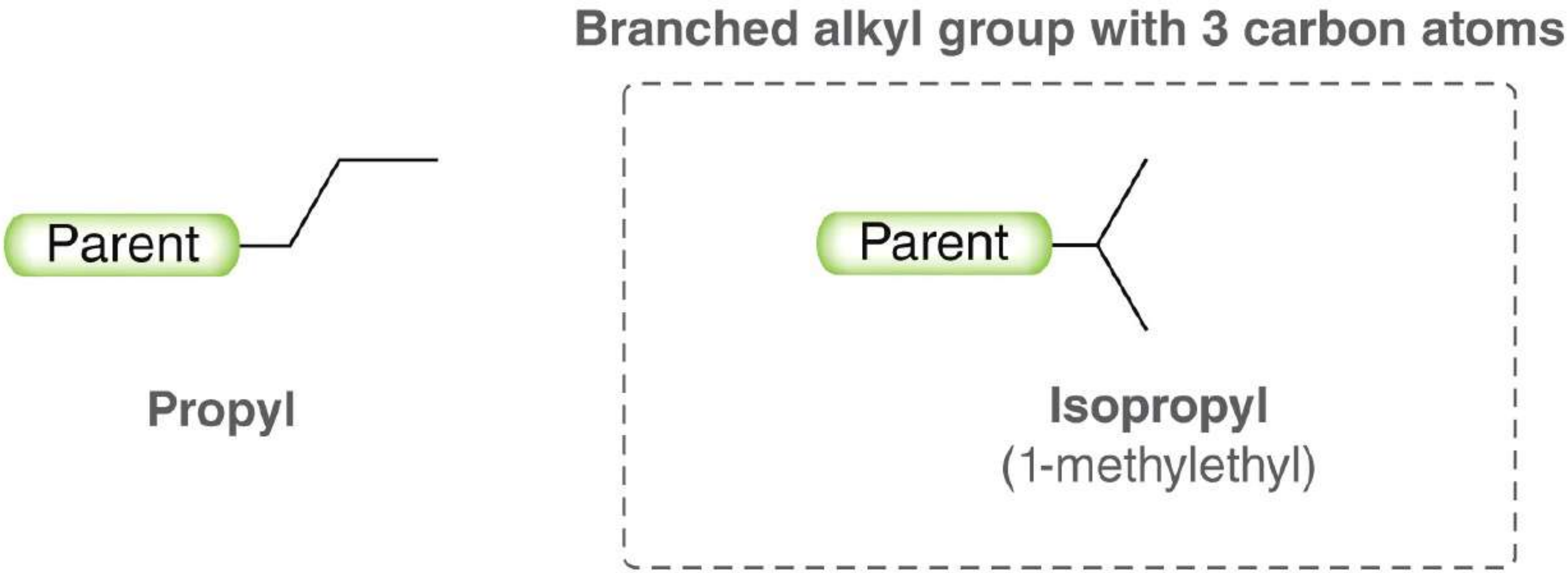


1. Number the longest carbon chain WITHIN the substituent. Start with the carbon directly attached to the main chain
2. Name the substituent (in this case butyl)
3. Name and Number the substituents side group (in this case 2-methyl)

- The name of the substituent is (2-methylbutyl)

4.2 Identifying Substituents

2. Identify substituents (side groups)
   - Some branched substituents have **common** names that you may want to memorize, because they are used more frequently than their IUPAC names

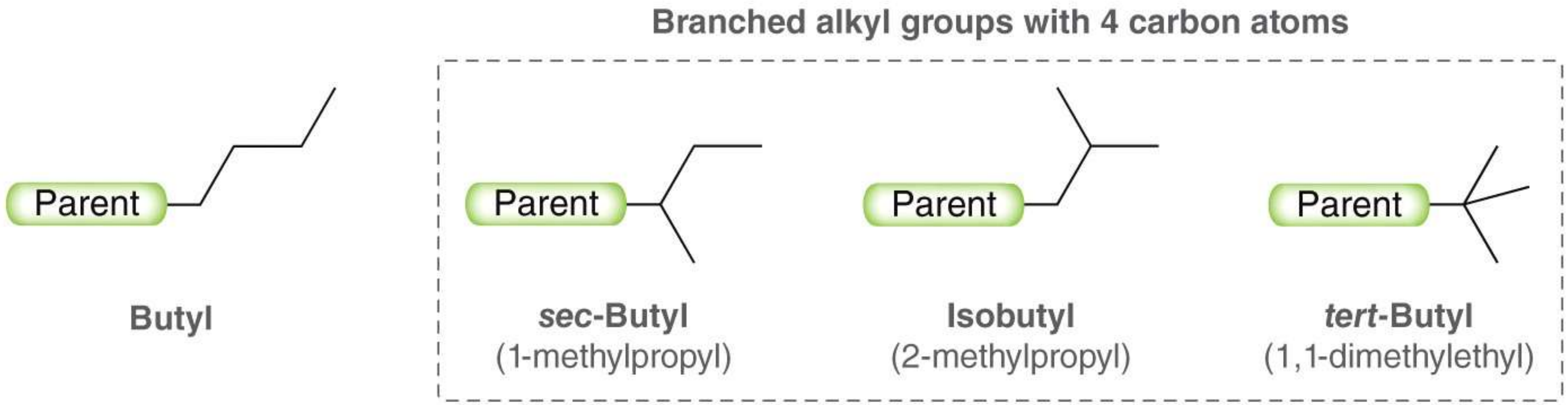


Propyl

Isopropyl
(1-methylethyl)

4.2 Identifying Substituents

2. Identify substituents (side groups)
   - Some branched substituents have **common** names that you may want to memorize



Butyl

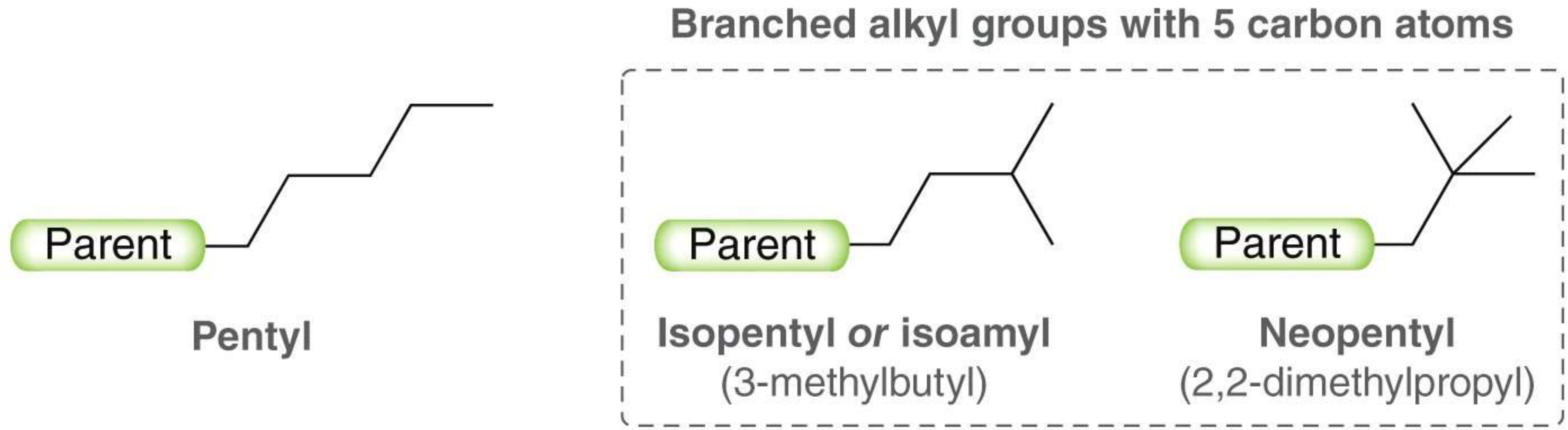
***sec*-Butyl**
(1-methylpropyl)

Isobutyl
(2-methylpropyl)

***tert*-Butyl**
(1,1-dimethylethyl)

4.2 Identifying Substituents

2. Identify substituents (side groups)
   - Some branched substituents have **common** names that you may want to memorize



Branched alkyl groups with 5 carbon atoms

Pentyl

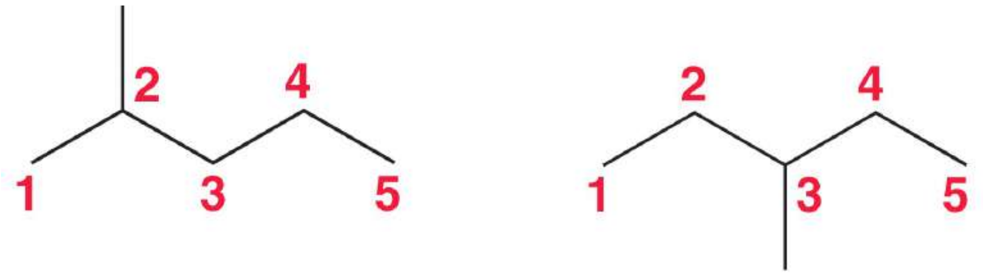
Isopentyl *or* isoamyl
(3-methylbutyl)

Neopentyl
(2,2-dimethylpropyl)

- Practice with SkillBuilder 4.3

4.2 Assembling The Entire Name

- Number in sequence the consecutive carbons in the parent chain
- The number or **locant** is used to communicate where each substituent is attached to the parent chain



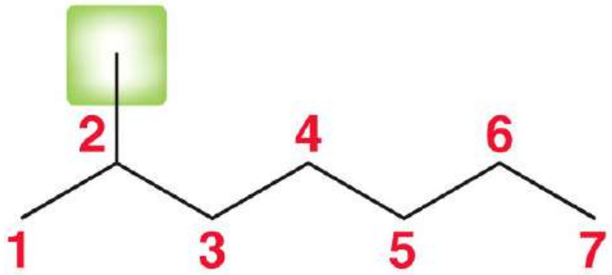
2-Methylpentane 3-Methylpentane

- The molecules above are isomers, and they have the same parent name. Their full name must differ though, because they are not identical

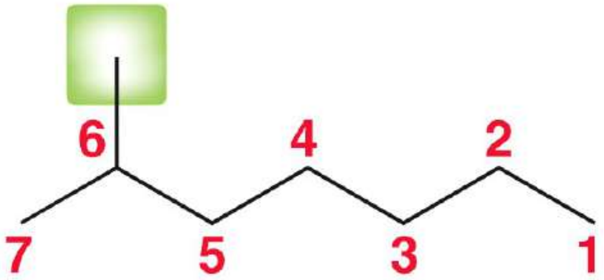
4.2 Assembling The Entire Name

- Guidelines to follow when numbering the parent chain
  1. If ONE substituent is present, number the parent chain so that the substituent has the lowest number possible

Correct

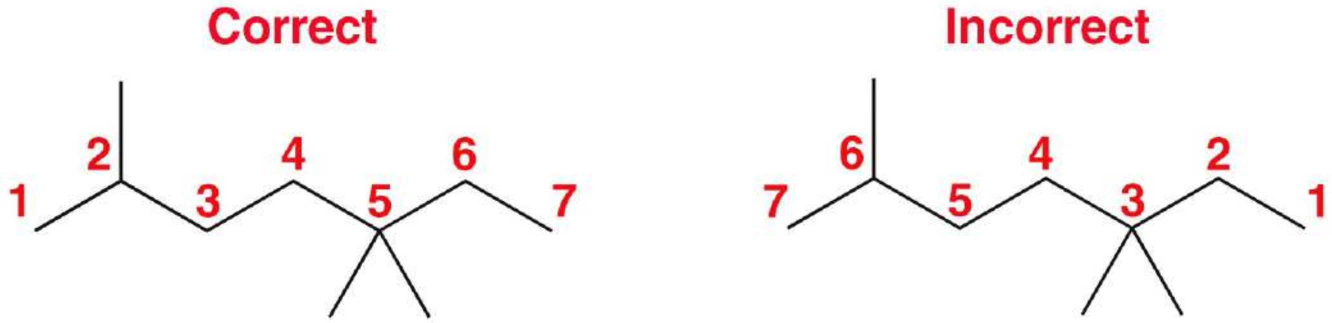


Incorrect



4.2 Assembling The Entire Name

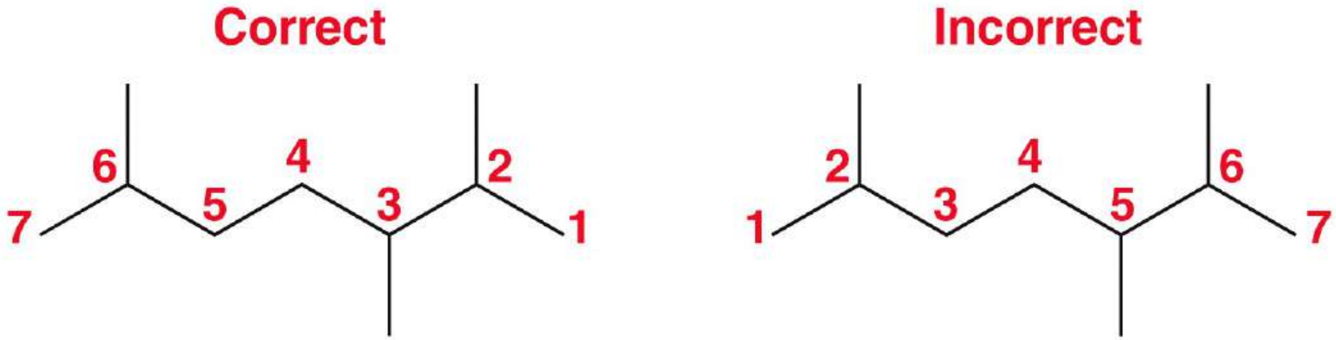
- Guidelines to follow when numbering the parent chain
  2. When multiple substituents are present, number the parent chain to give the first substituent the lowest number possible



2, 5 , 5 beats **3**, 3 , 6

4.2 Assembling The Entire Name

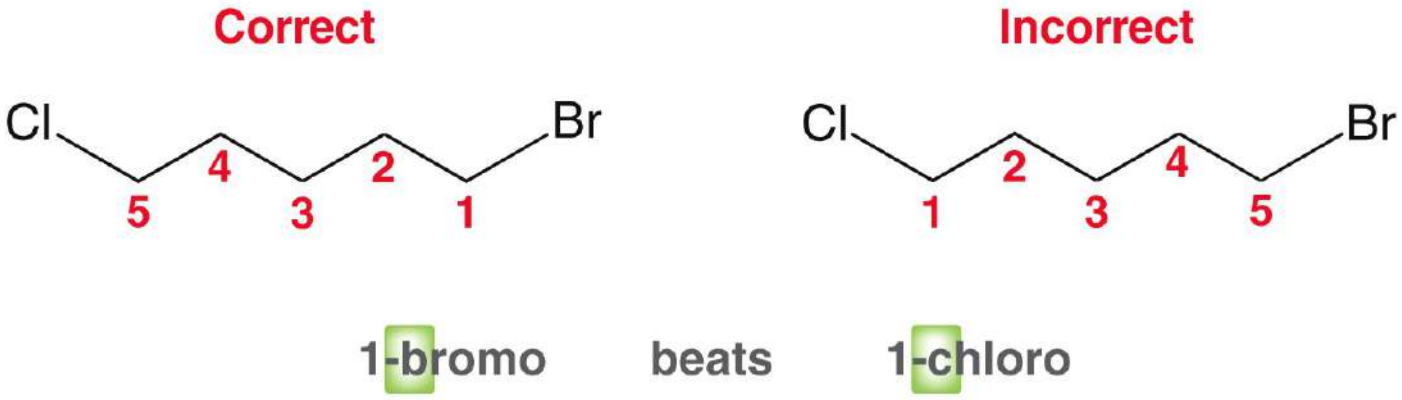
- Guidelines to follow when numbering the parent chain
  3. If there is a tie, then number the parent chain so that the second locant gets the lowest number possible



2, 3, 6 beats 2, 5, 6

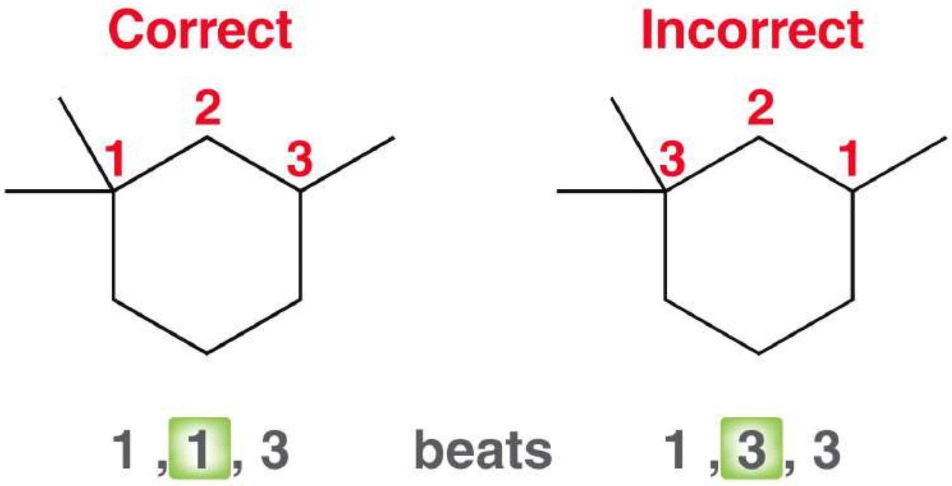
4.2 Assembling The Entire Name

- Guidelines to follow when numbering the parent chain
  4. If there is no other tie-breaker, then assign the lowest number alphabetically



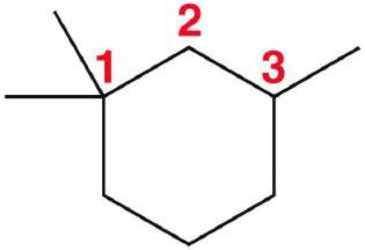
4.2 Assembling The Entire Name

- Guidelines to follow when numbering the parent chain
  - The same rules apply for cycloalkanes



4.2 Assembling The Entire Name

- Guidelines to follow when numbering the parent chain
  5. To assemble the complete name, assign a locant to each substituent, and list them before the parent chain name in alphabetical order
  6. A prefix is used (di, tri, terta, penta, etc.) if multiple substituents are identical
  7. Prefixes are NOT used for alphabetical purposes, except for the prefix "iso"
- Name the cycloalkane:



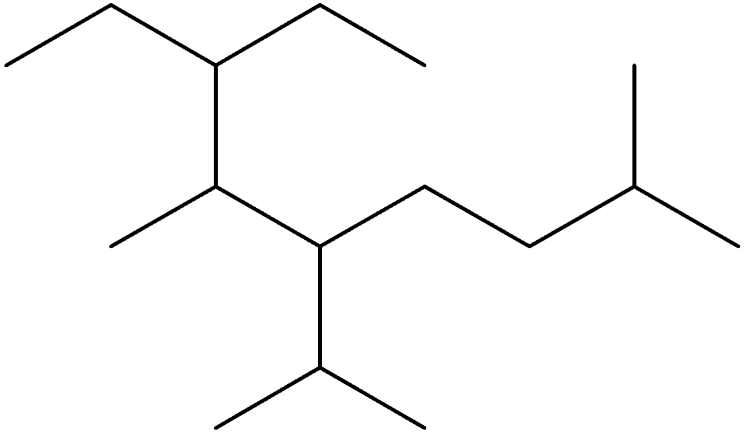
4.2 Naming Alkanes Summary

1. Identify the parent chain (the longest consecutive chain of carbons)
2. Identify and Name the substituents
3. Number the parent chain and assign a locant (and prefix if necessary) to each substituent
    - Give the first substituent the lowest number possible
4. List the numbered substituents before the parent name in alphabetical order
    - Ignore prefixes (except iso) when ordering alphabetically

- Practice with SkillBuilder 4.4

4.2 Naming Alkanes Summary

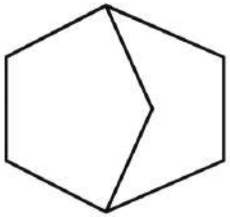
- Name the following molecule



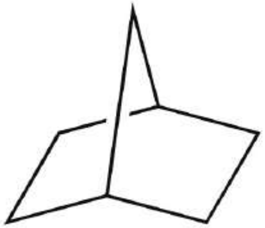
- Draw the bond-line representation for 1-*tert*-butyl-3-cyclopentyl-2-ethyl-4-methylcyclohexane

4.2 Naming Bicyclic Compounds

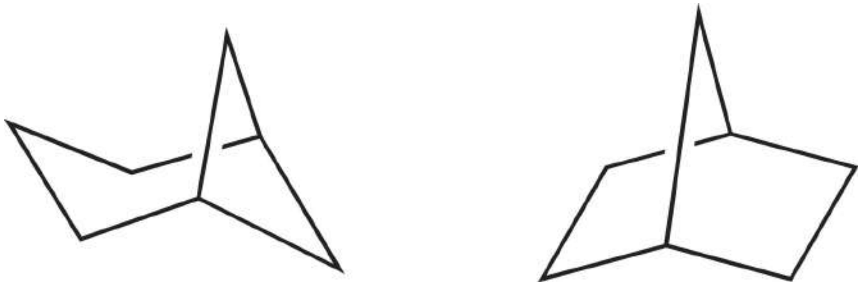
- There are many compounds with two fused rings called bicyclic compounds



is the same as

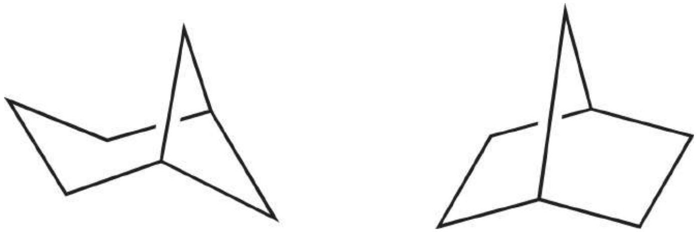


- To name a bicyclic compound, include the prefix bicyclo in front of the normal name ending in -ane. For example, the compounds below could both be named, bicycloheptane



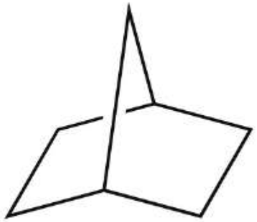
4.2 Naming Bicyclic Compounds

- Yet we know that if two molecules are not identical, they can not have the same exact name
- What is the difference between the two compounds below?



- The number of carbons connecting the bridgeheads is different. Count them.

Bicyclo[3.1.1]heptane

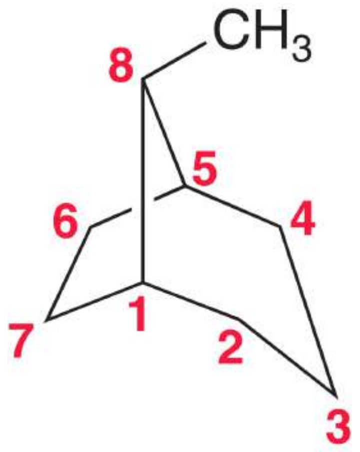


Bicyclo[2.2.1]heptane

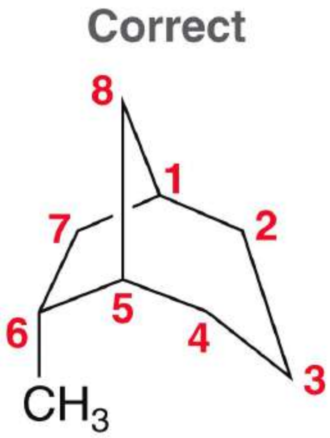
4.2 Naming Bicyclic Compounds

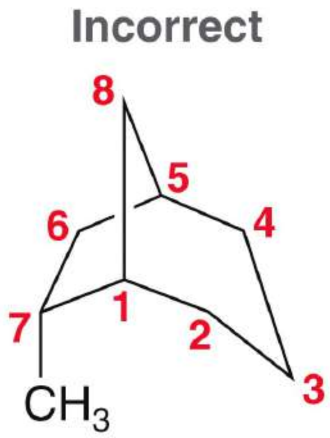
1. To number the bicyclo parent chain, start at a bridgehead carbon and number the longest carbon chain connecters first

- What numbering would result if we started from the other bridgehead?



2. Without violating rule 1 above, give the substituents the lowest numbers possible

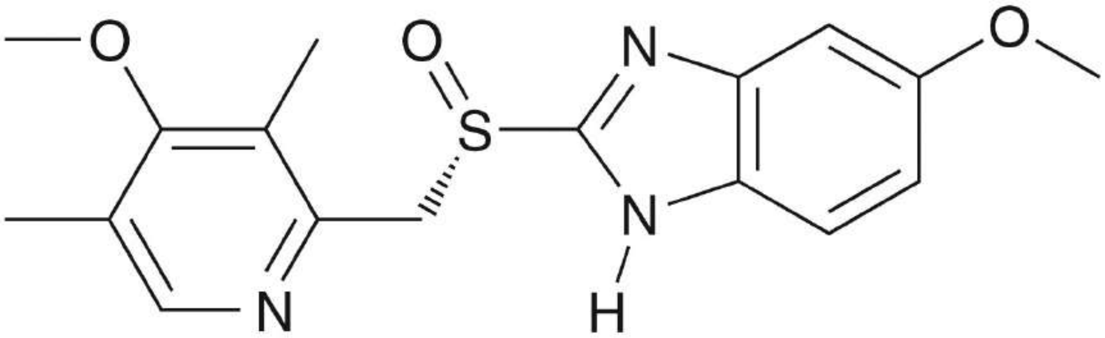




- Practice with SkillBuilder 4.5

4.2 Naming Compounds

- For molecules that are large and complex, there are MANY more rules to follow using the IUPAC system
- Just pronouncing the name of this molecule is difficult



(*S*)-5-Methoxy-2-[(4-methoxy-3,5-dimethyl pyridin-2-yl)methylsulfinyl]-3*H*-benzoimidazole

- Often trade names are used for the sake of simplicity
- The molecule above is also known as esomeprazole or Nexium, which is a drug for acid reflux

4.3 Constitutional Isomers

- Recall that isomers are different structures made from the same atoms
- Isomers are NOT identical, but they have the same formula
- Constitutional isomers differ in connectivity
- Consider two of the five constitutional isomers for hexane

- Draw the other three C_6H_{14} constitutional isomers

4.3 Constitutional Isomers

- The number of different possible ways to connect atoms increases dramatically when there are more atoms.
- Consider Table 4.4

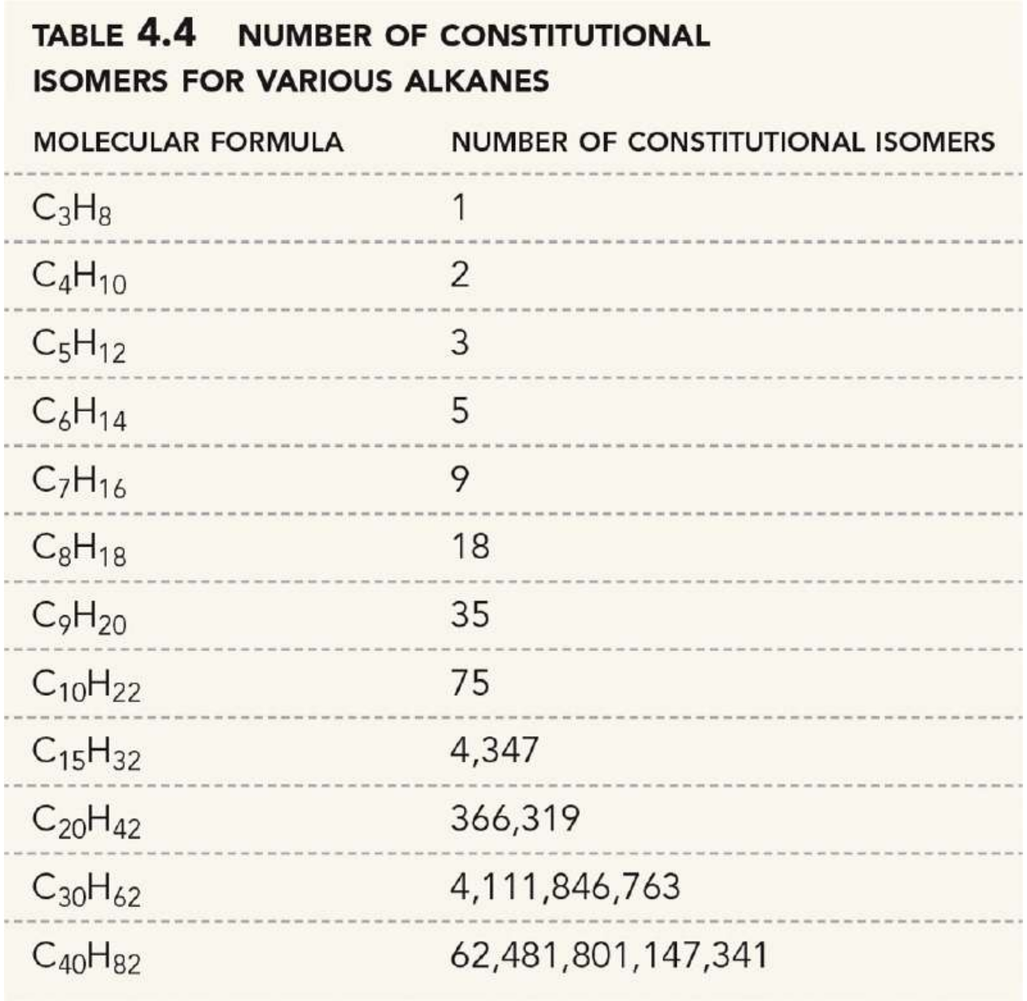
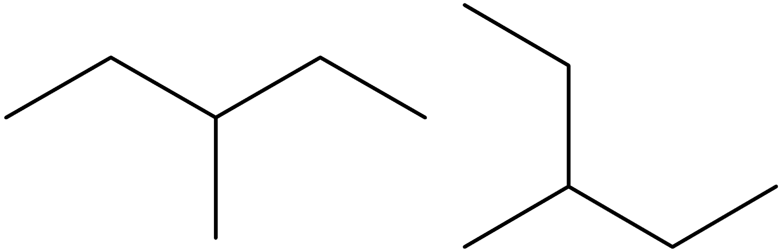


TABLE 4.4 NUMBER OF CONSTITUTIONAL ISOMERS FOR VARIOUS ALKANES

MOLECULAR FORMULA	NUMBER OF CONSTITUTIONAL ISOMERS
C_3H_8	1
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

4.3 Constitutional Isomers

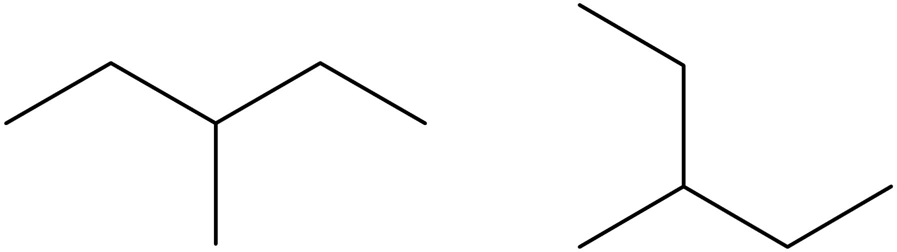
- How can you recognize if two molecules are isomers?
- Are these two structures isomers? Do they have the same formula?

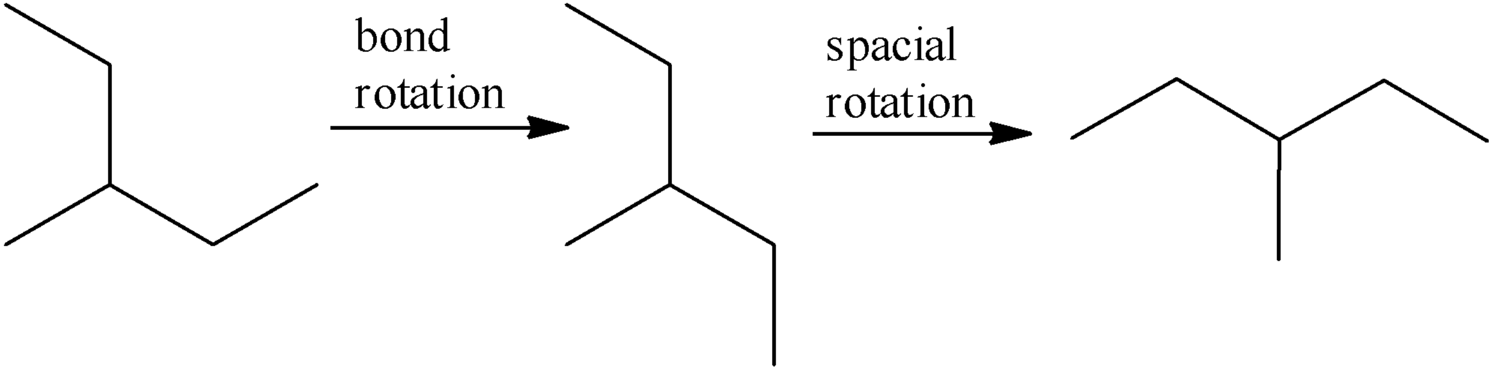


- If they have the same formula, they may be isomers or they may be identical
- You can test if they are identical using two methods
  1. Flip one of the molecules in 3D space and rotate around its single bonds until it is super-imposable on the other molecule
  2. Name them. If they have the same name, they are identical

4.3 Constitutional Isomers

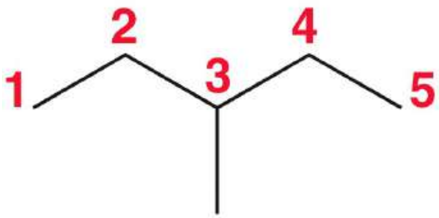
- You can test if they are identical using two methods
  1. Flip one of the molecules in 3D space and rotate around its single bonds until it is super-imposable on the other molecule



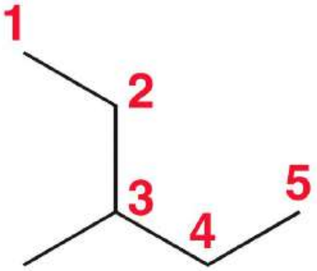


4.3 Constitutional Isomers

- You can test if they are identical using two methods
  2. If they have the same name, they are identical



3-Methylpentane



3-Methylpentane

- Which method for testing whether molecules are identical is probably more sure-fire?

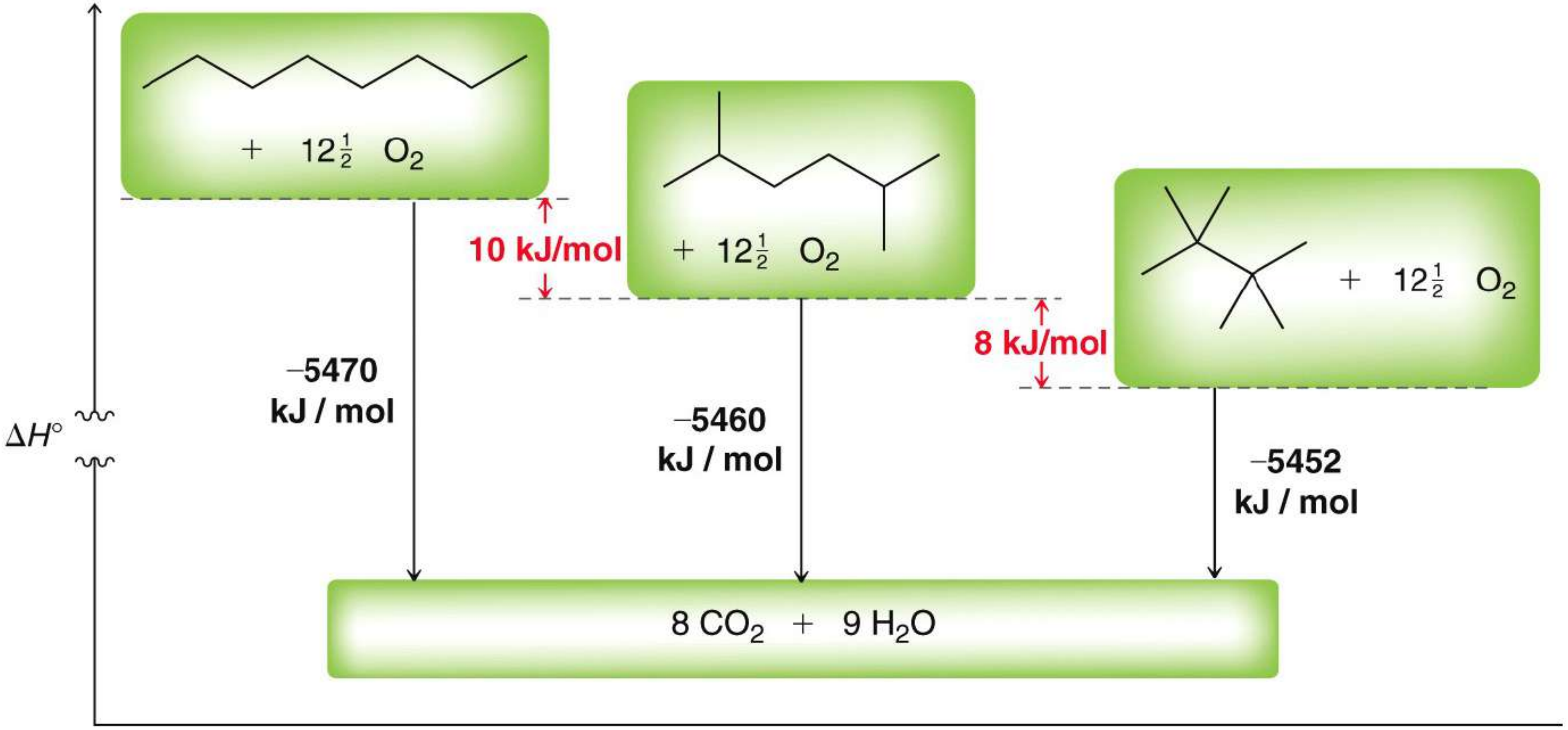
- Practice with SkillBuilder 4.6

4.4 Relative Stability of Isomers

- To rationalize and predict the outcomes of chemical reactions, it is helpful to assess stability of compounds
- Remember: stable = low potential energy = low reactivity = little energy will be released upon reacting
- If you drove a car today, what chemical reaction with alkanes did you perform?
- What is the general reaction equation for combustion?

4.4 Relative Stability of Isomers

- Compare the heats of combustion for 3 octane isomers



4.5 Sources and Uses of Alkanes

- Petroleum, which literally means rock oil is the main source of alkanes
- Petroleum is a mixture of hundreds of hydrocarbons, mostly alkanes with varying numbers of carbons and varying degrees of branching
- The alkanes in petroleum with 5 to 12 carbons per molecule are most valuable, and they can be separated from the rest of the oil by distillation
- HOW does distillation work?

4.5 Sources and Uses of Alkanes

- Table 4.5 shows the various components of petroleum

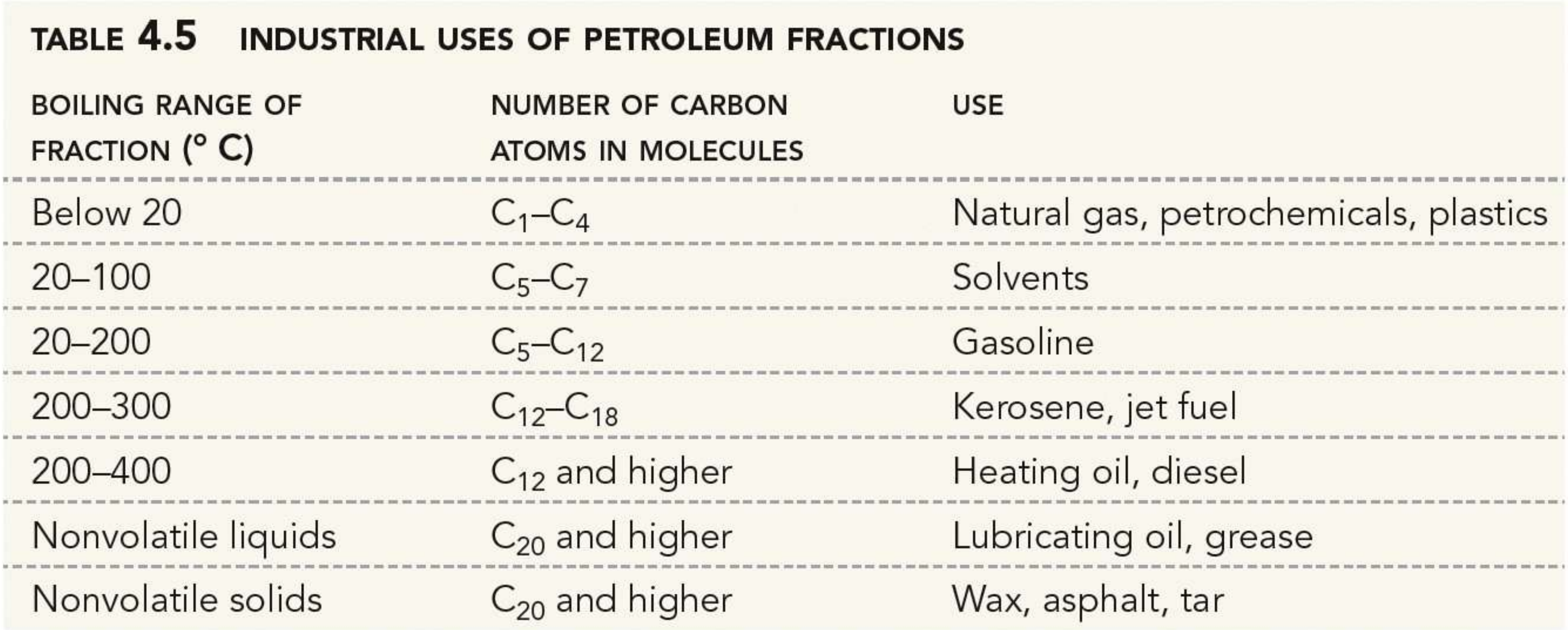


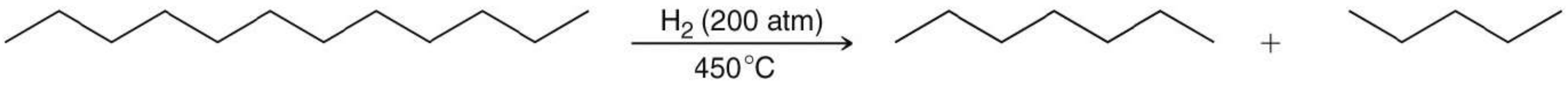
TABLE 4.5 INDUSTRIAL USES OF PETROLEUM FRACTIONS

BOILING RANGE OF FRACTION (° C)	NUMBER OF CARBON ATOMS IN MOLECULES	USE
Below 20	C_1–C_4	Natural gas, petrochemicals, plastics
20–100	C_5–C_7	Solvents
20–200	C_5–C_{12}	Gasoline
200–300	C_{12}–C_{18}	Kerosene, jet fuel
200–400	C_{12} and higher	Heating oil, diesel
Nonvolatile liquids	C_{20} and higher	Lubricating oil, grease
Nonvolatile solids	C_{20} and higher	Wax, asphalt, tar

- The gasoline fraction of crude oil only makes up about 19%, which is not enough to meet demand

4.5 Sources and Uses of Alkanes

- Gasoline is a mixture of straight, branched, and aromatic hydrocarbons (5-12 carbons in size)
- Large alkanes can be broken down into smaller molecules by *Cracking*



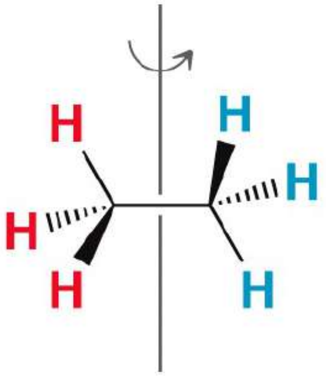
- Straight chain alkanes can be converted into branched alkanes and aromatic compounds through *Reforming*
- After using these processes, the yield of gasoline is about 47% rather than 19%

4.5 Sources and Uses of Alkanes

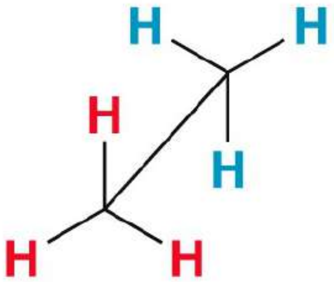
- At room temperature
  - Small alkanes with 1-4 carbons are gasses
  - Medium size alkanes with 5-12 carbons are liquids
  - Large alkanes with 13-20 carbons are oils
  - Extra large alkanes with 20-100 carbons are solids like tar and wax
  - Super-sized alkanes called polymers can have thousands or millions of carbon atoms in each molecule
- What type of properties would you expect such polymers to possess?
- Why? Consider London forces

4.6 Newman Projections

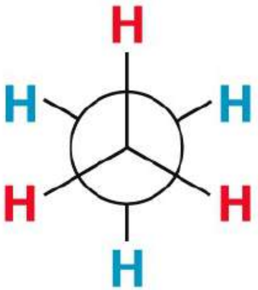
- We know that single bonds in molecules can rotate
- Different rotational states are called **conformations**
- 3D Rotational conformations are difficult to represent on a 2D paper. Its useful to make a molecular model to help you visualize the structures
- Here are three ways to represent ethane



Wedge and dash



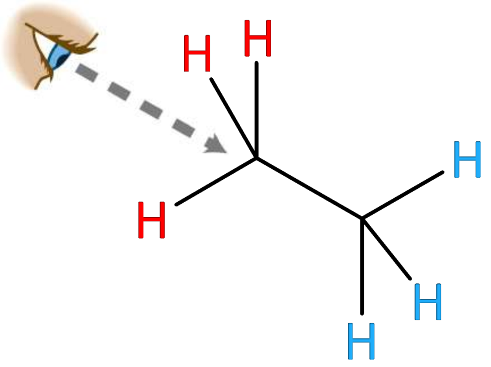
Sawhorse

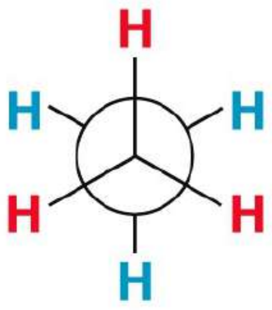


Newman projection

4.6 Newman Projections

- Look directly down the C-C single bond axis. This is where it is especially helpful to have a model
- The front carbon should eclipse the single bond and the carbon behind it
- Show the front carbon as a point and the back carbon as a large circle behind it



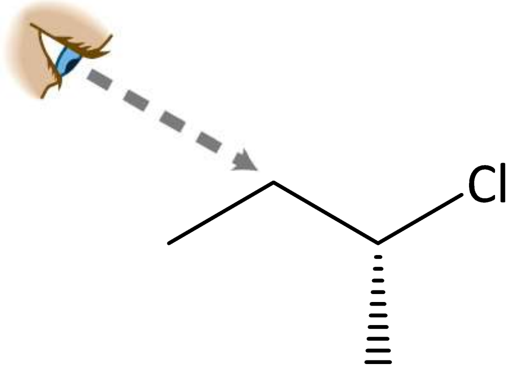


Newman projection

- Practice with SkillBuilder 4.7

4.6 Newman Projections

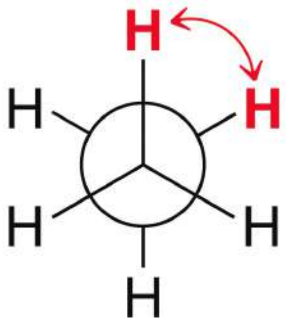
- Draw a Newman projection for the following molecule



- How would it look if the observer were viewing it from the opposite direction?

4.7 Rotational Conformations

- What is the angle between H atoms on the same carbon? In the Newman projection it looks like 120°.
- Does the angle affect stability? WHY? Think about areas of high electron density repelling
- The angle between H atoms on adjacent carbons is called a dihedral or **torsional** angle. It is 60° in the molecule below

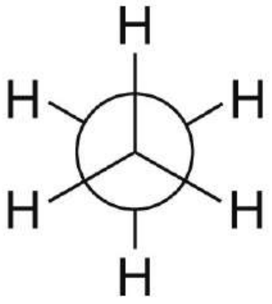


Dihedral angle = 60°

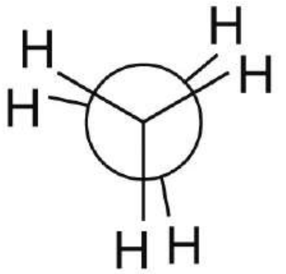
WILEY

4.7 Rotational Conformations

- If ethane were to rotate 60° about the C-C bond, the the H atoms on adjacent carbons eclipse one another
- Compare the stability of the eclipsed and staggered conformations based on the repulsion of areas of high electron density



Staggered conformation
Lowest in energy

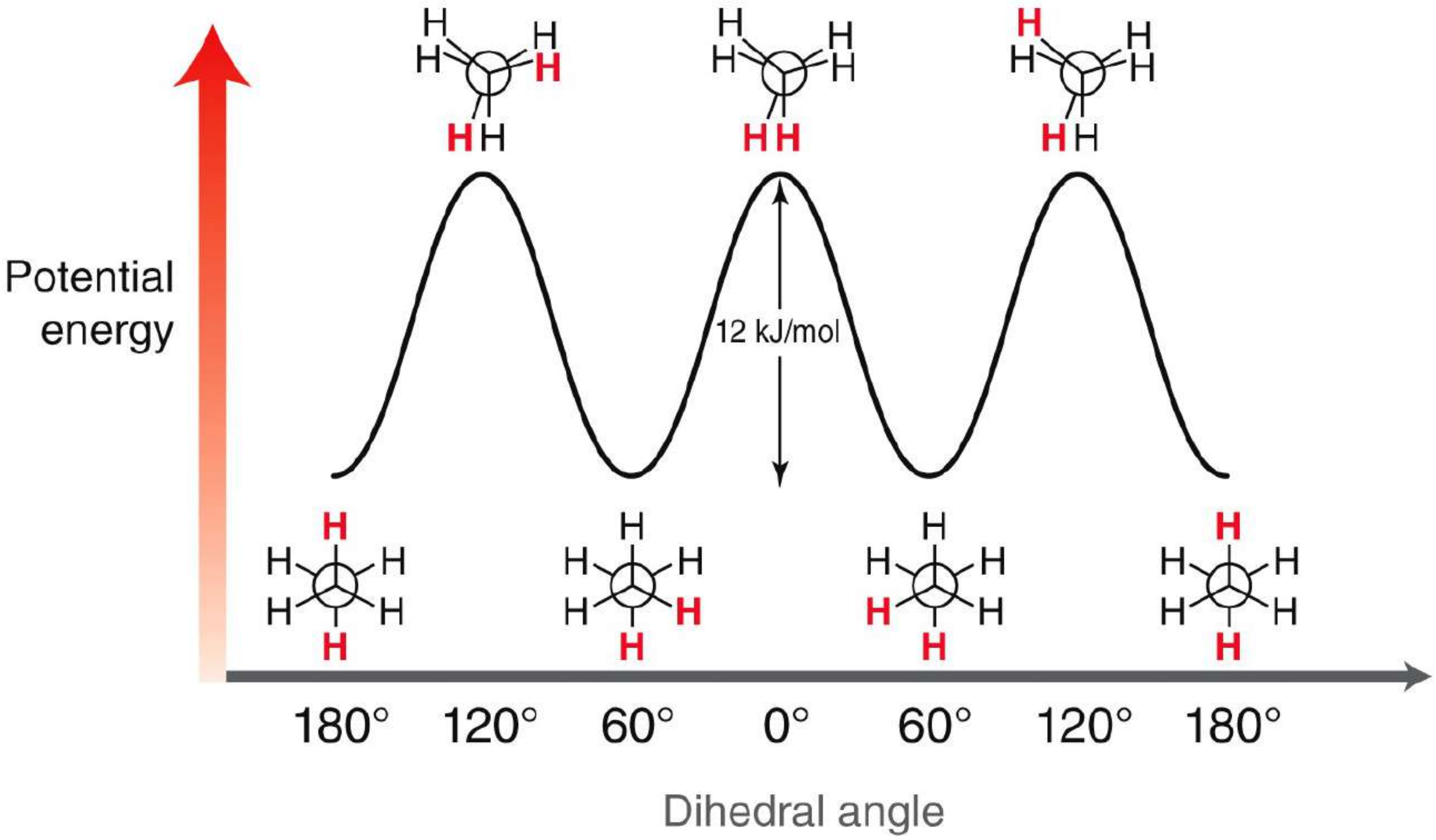


Eclipsed conformation
Highest in energy

- What other conformations are possible?

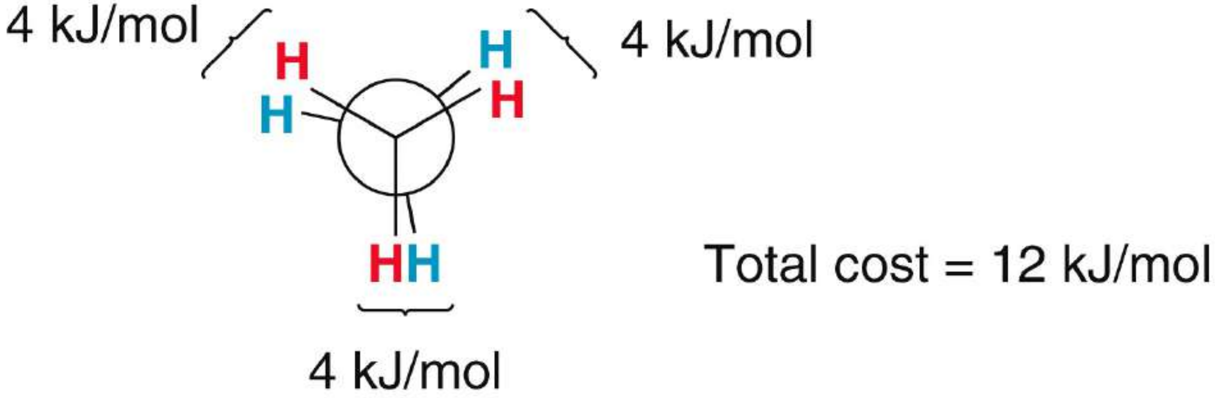
4.7 Rotational Conformations

- Consider a complete 360° rotation about the C-C bond



4.7 Rotational Conformations

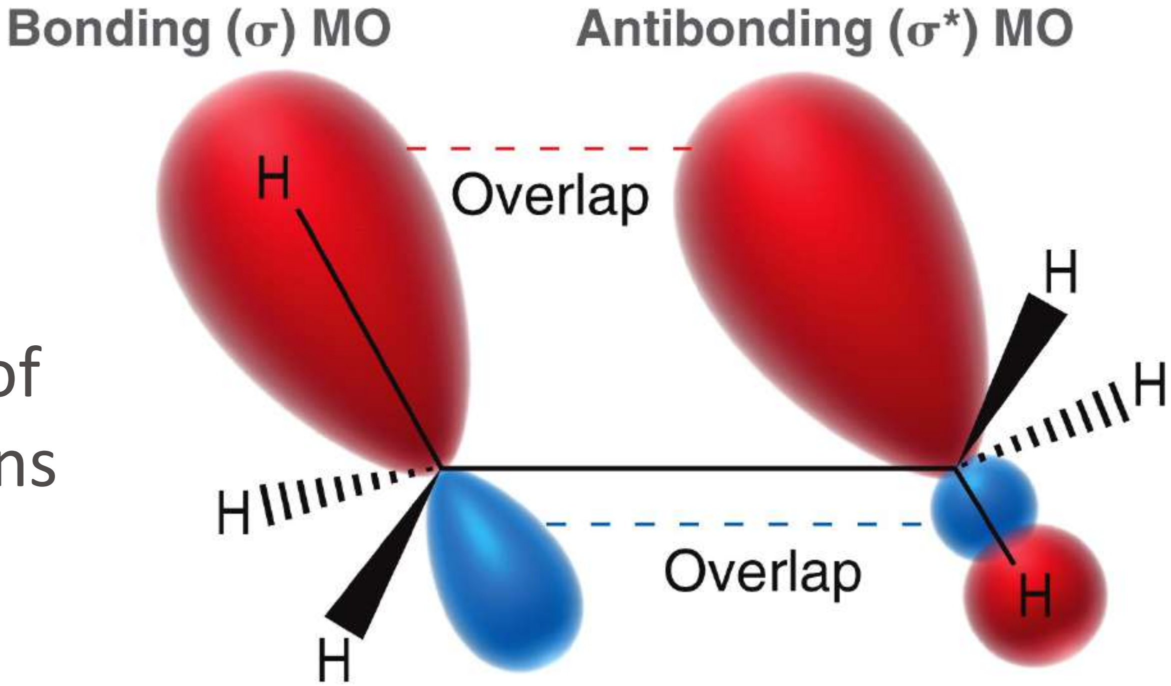
- The difference in energy between the staggered and eclipsed conformations is called **torsional strain**
- With a difference of 12 kJ/mol in stability, at room temperature, 99% of the molecules will be in the staggered conformation



- How would the ratio change at a higher temperature?

4.7 Rotational Conformations

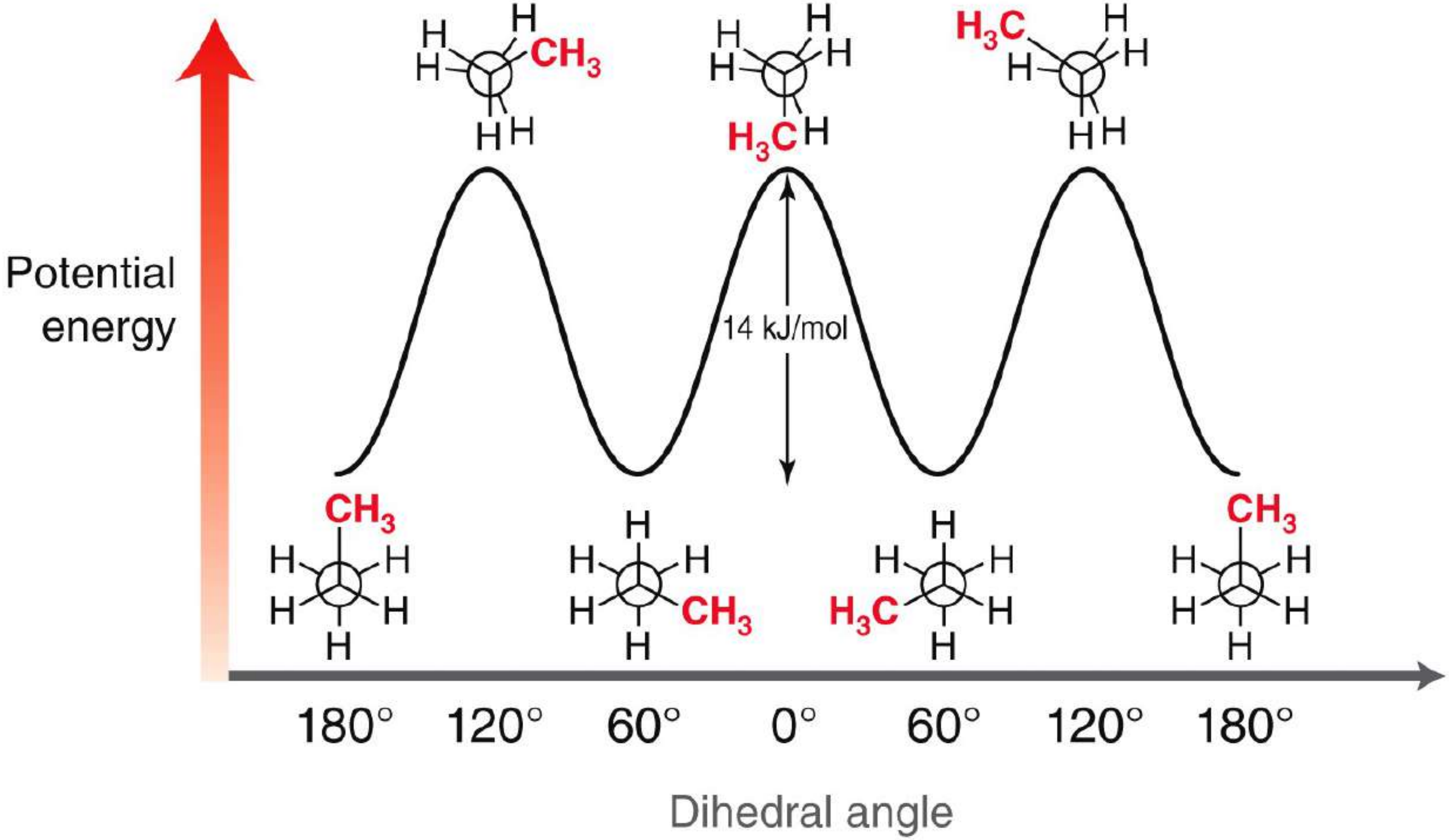
- **Torsional strain** can also be explained using molecular orbital theory
- In the staggered conformation, the bonding and antibonding MOs of neighboring carbons overlap



WILEY

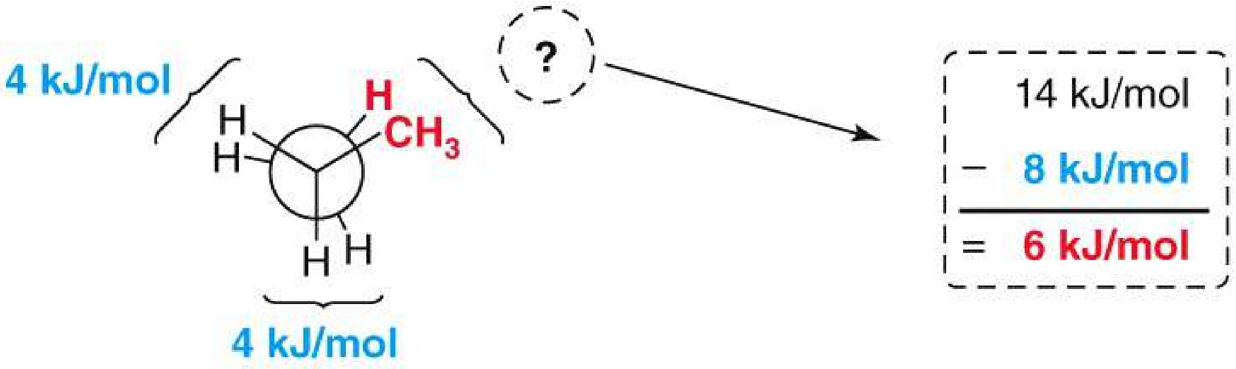
4.7 Rotational Conformations

- The analysis of **torsional strain** for propane shows a very similar situation



4.7 Rotational Conformations

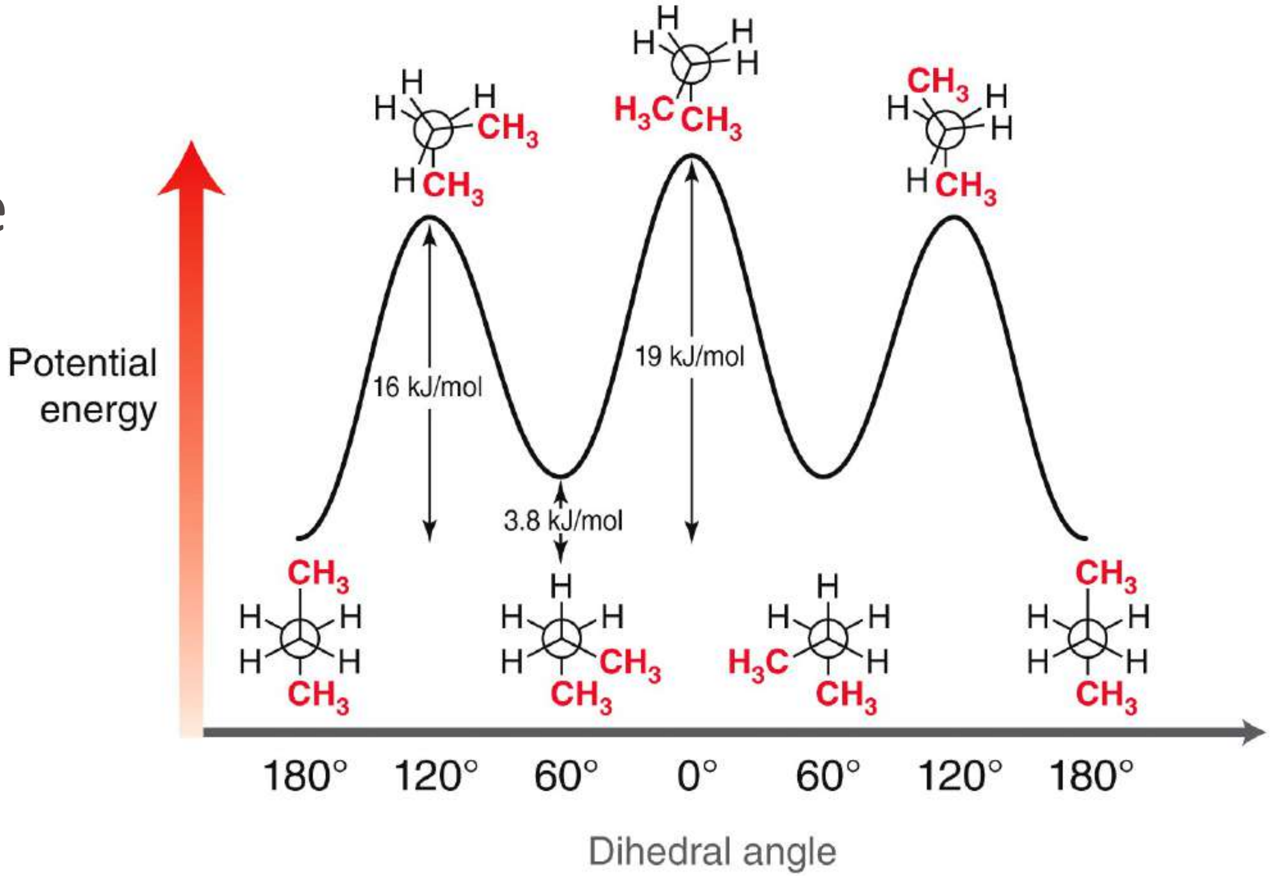
- The **torsional strain** for propane is 14 kJ/mol, which is 2 kJ/mol more than for ethane
- If each H-----H eclipsing interaction costs 4 kJ/mol of stability, that total can be subtracted from the total 14 kJ/mol to calculate the contribution of a CH_3-----H eclipsing interaction



- Practice with conceptual checkpoint 4.19

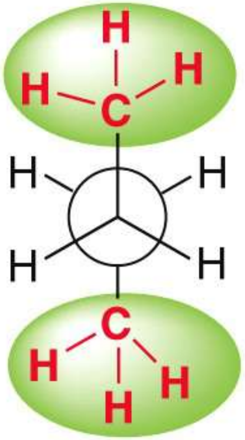
4.8 Butane's Conformations

- The analysis of **torsional strain** for butane shows more variation
- Note that there are multiple staggered conformations and multiple eclipsed conformations



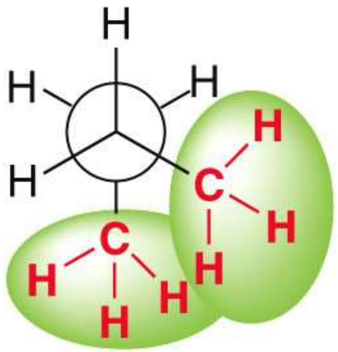
4.8 Butane’s Conformations

- The stability of the different staggered conformations differs by 3.8 kJ/mol
- The anti conformation has less steric hindrance.



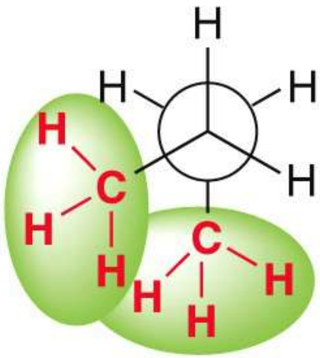
Anti

Methyl groups are farthest apart



Gauche

Methyl groups experience a gauche interaction

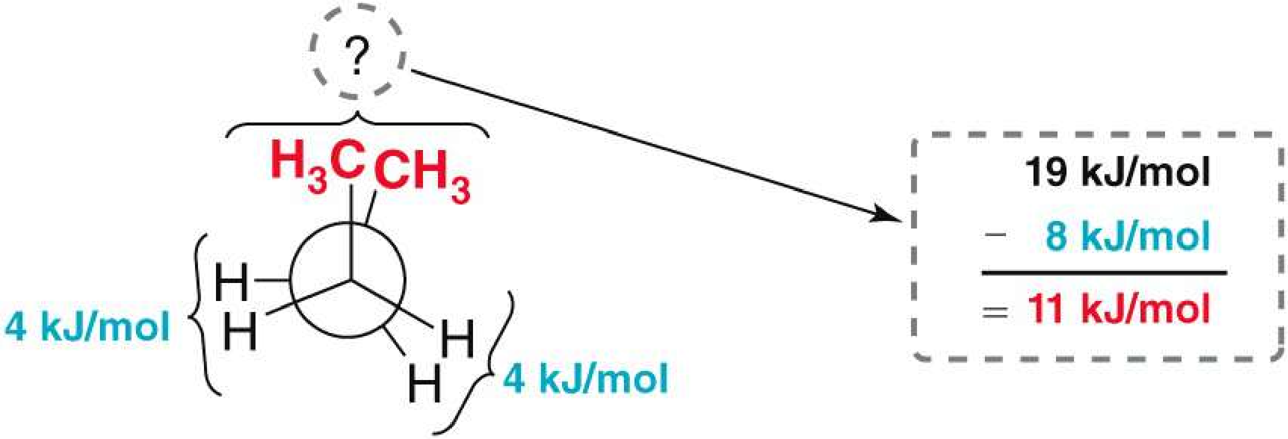


Gauche

Methyl groups experience a gauche interaction

4.8 Butane's Conformations

- The least stable conformation results when the methyl groups eclipse one another



- Each CH_3-----CH_3 **eclipsing** interaction accounts for 11 kJ/mol of energy (torsional and steric strain).

4.8 Butane's Conformations

- The values in Table 4.6 can be used to predict relative energies for various conformations
- Practice with SkillBuilder 4.8

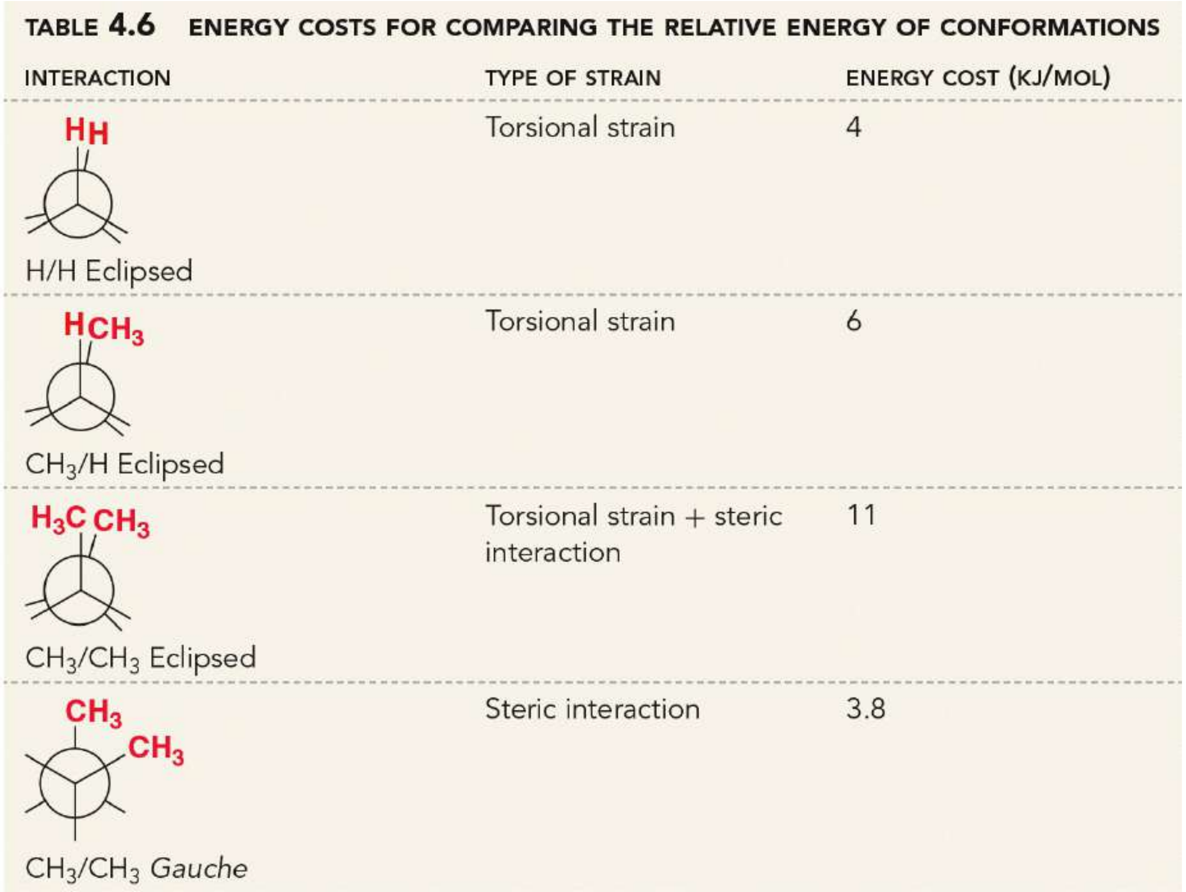


TABLE 4.6 ENERGY COSTS FOR COMPARING THE RELATIVE ENERGY OF CONFORMATIONS

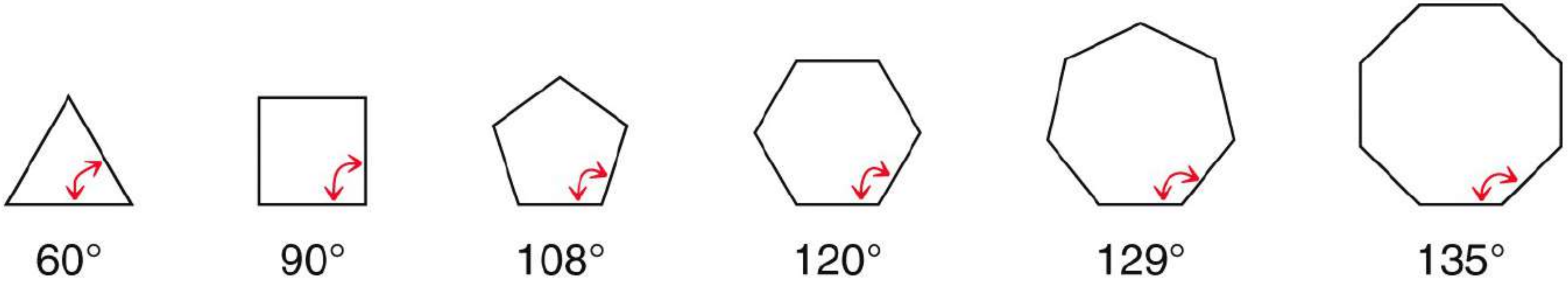
INTERACTION	TYPE OF STRAIN	ENERGY COST (KJ/MOL)
H/H Eclipsed	Torsional strain	4
CH_3/H Eclipsed	Torsional strain	6
CH_3/CH_3 Eclipsed	Torsional strain + steric interaction	11
CH_3/CH_3 *Gauche*	Steric interaction	3.8

4.8 Rotational Conformations

- Draw a Newman projection for the highest and lowest energy conformations for 2,2,3,4,4-pentamethylhexane viewing the Newman projection down the C_3-C_4 axis

4.9 Cyclic Alkanes

- Carbon atoms in alkanes are sp^3 hybridized
- What bond angles are optimal for such carbons?
- If cycloalkanes were flat, what bond angles would be expected?



- To optimize the bond angles, most cycloalkanes are NOT flat in their most stable conformation

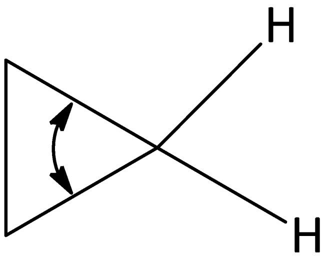
4.9 Cyclic Alkanes

- Why are heats of combustion reported per CH_2 group?
- Considering the data in Table 4.7, which ring has the least **ring strain**?

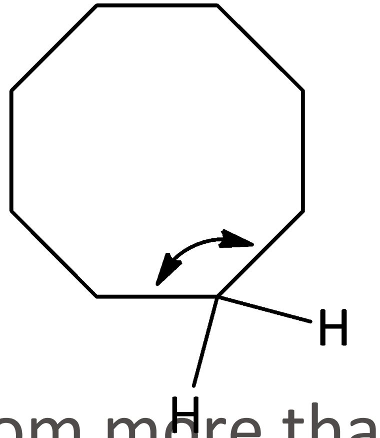
CYCLOALKANE	NUMBER OF CH_2 GROUPS	HEAT OF COMBUSTION PER CH_2 GROUP (KJ / MOL)
Cyclopropane	3	697
Cyclobutane	4	680
Cyclopentane	5	658
Cyclohexane	6	653
Cycloheptane	7	657
Cyclooctane	8	658
Cyclononane	9	659
Cyclodecane	10	659
Cycloundecane	11	661
Cyclododecane	12	654

4.9 Cyclic Alkanes

- Why does it make a molecule less stable to have angles less than 109.5°?



- Why does it make a molecule less stable to have angles greater than 109.5°?

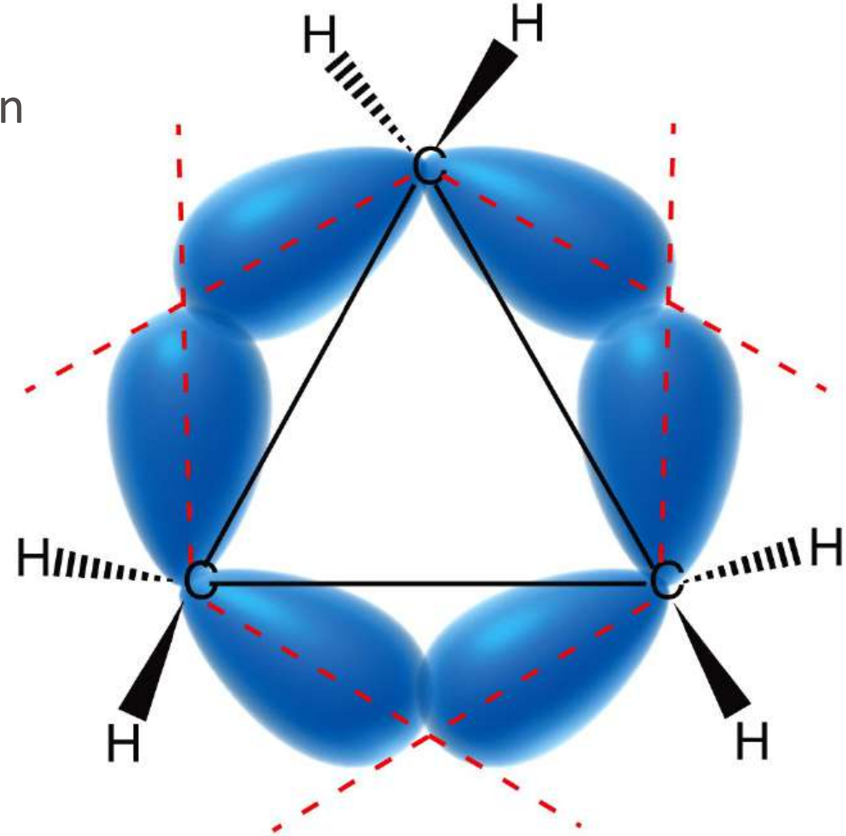


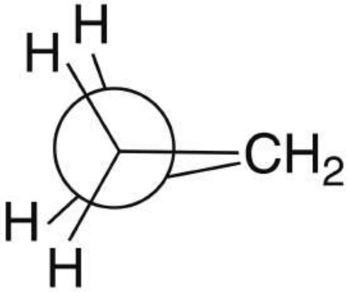
- **Ring strain** results from more than just angle strain

4.9 Cyclopropane

- Cyclopropane is 44 kJ/mol less stable than cyclohexane per CH_2 group. It is highly strained and very reactive

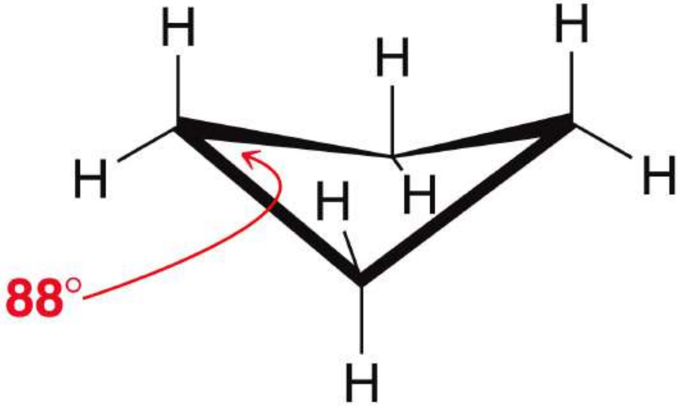
1. Angle strain
    - Bond angles of 60° cause electron pair repulsion in adjacent bonds
    - Inefficient sigma bond overlap
2. Torsional strain – eclipsing C-H bonds all the way around the ring – see the Newman projection





4.9 Cyclobutane

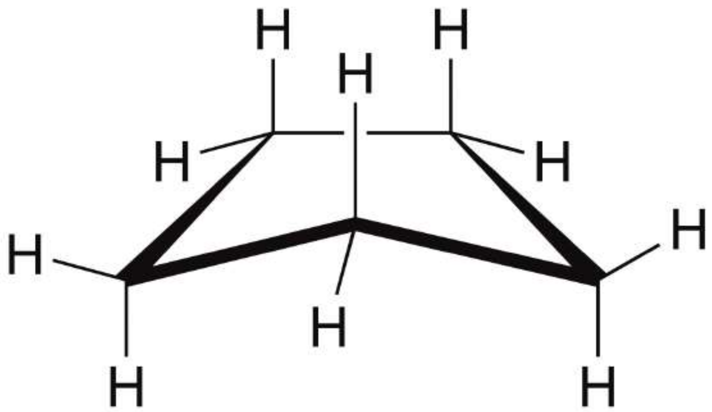
- Cyclobutane is 27 kJ/mol less stable than cyclohexane per CH_2 group. It is also strained and reactive
  1. Angle strain results from bond angles of 88°, although it is not as severe as the 60° angles in cyclopropane
  2. Slight torsional strain results because adjacent C-H bonds are neither fully eclipsed nor fully staggered



- Why does it adopt a puckered conformation?

4.9 Cyclopentane

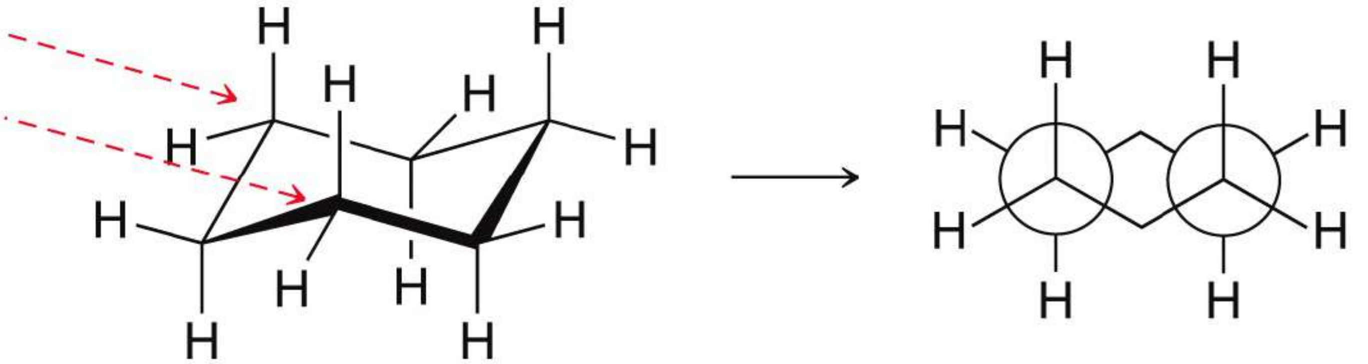
- Cyclopentane is only 5 kJ/mol less stable than cyclohexane per CH_2 group
  1. Angles are close to the optimal value
  2. Identify the minimal but significant torsional strain in the structure. It is very helpful to use a handheld model



- Why does it adopt the envelope conformation rather than a flat conformation?

4.10 Cyclohexane

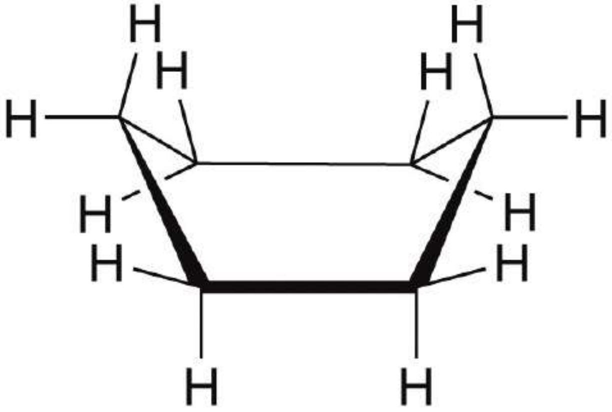
- Cyclohexane is considered to have ZERO ring strain in its optimal conformation, THE CHAIR
  1. No angle strain - angles must be 109.5°
  2. No torsional strain - all adjacent C-H bonds must be staggered


Look down both of these bonds simultaneously

- It helps to make a model as a visual aid! WHY is this called THE CHAIR?

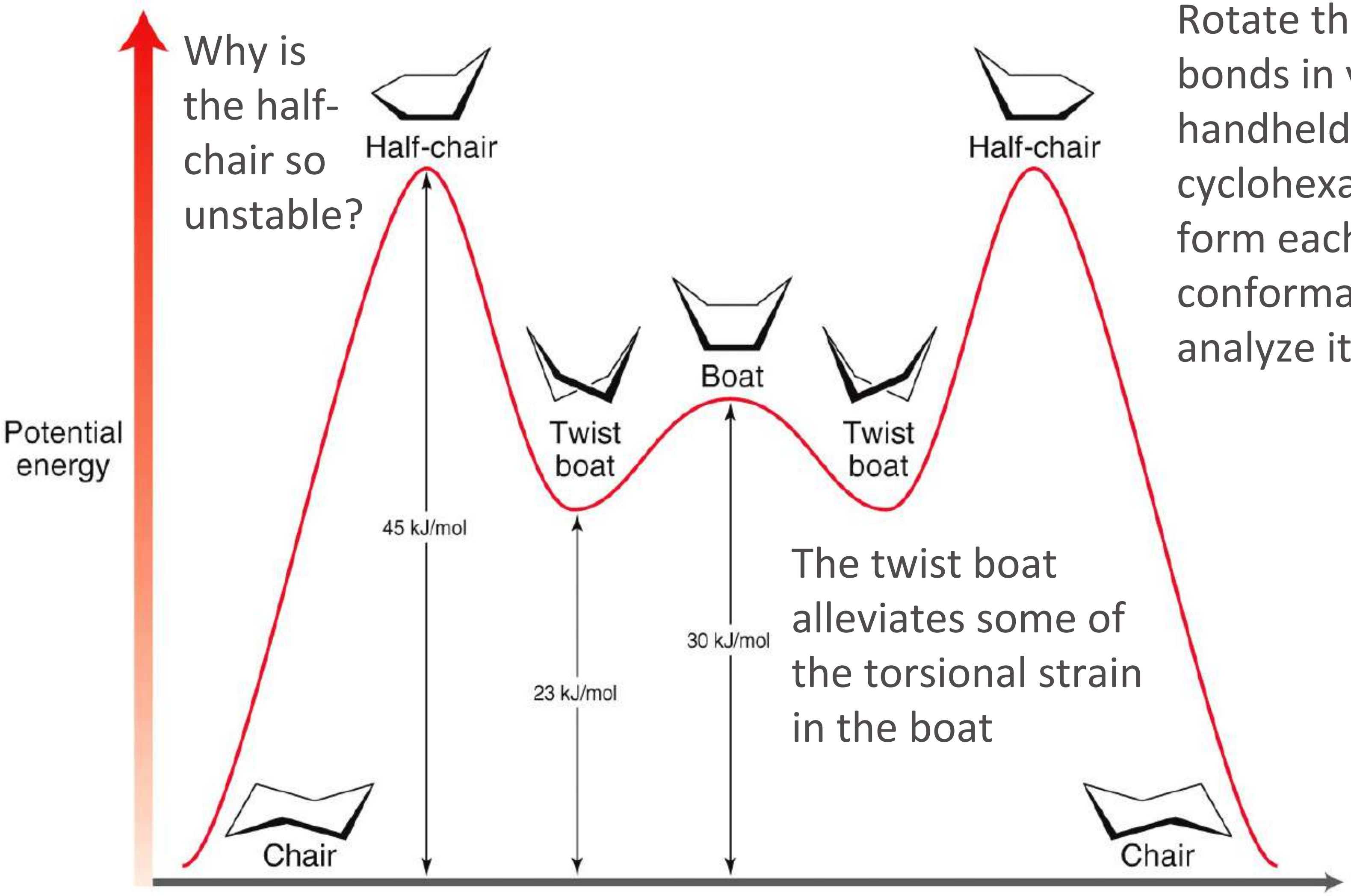
4.10 Cyclohexane

- Other conformations of hexane exist but are a bit less stable. Consider THE BOAT
  1. No angle strain - angles are 109.5°
  2. Torsional strain.
     - Use a molecular model to identify all four pairs of eclipsing C-H bonds
     - Draw a Newman projection that illustrates the torsional strain
  3. Steric strain – flagpole interactions. WHERE?



- Why is this conformation called the BOAT?

4.10 Cyclohexane



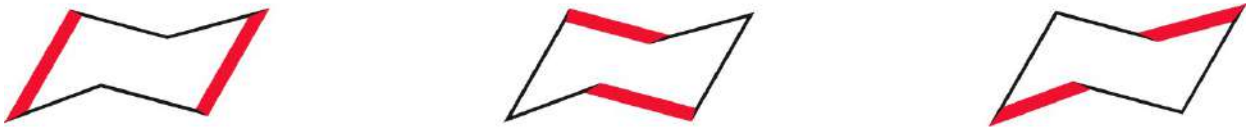
Why is the half-chair so unstable?

Rotate the C-C single bonds in your handheld cyclohexane model to form each of the conformations and analyze its energy

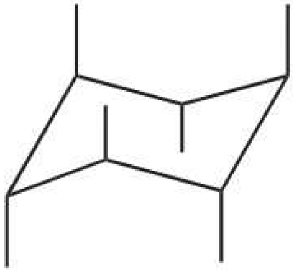
The twist boat alleviates some of the torsional strain in the boat

4.11 Drawing Chairs

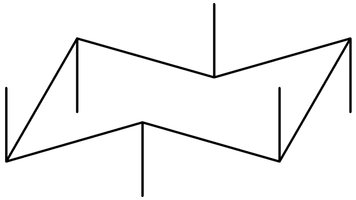
- It is critical to draw a CHAIR properly. Use three sets of parallel lines



- SIX of the atoms attached to the chair are axial. Axial groups point straight up and down alternating around the ring.



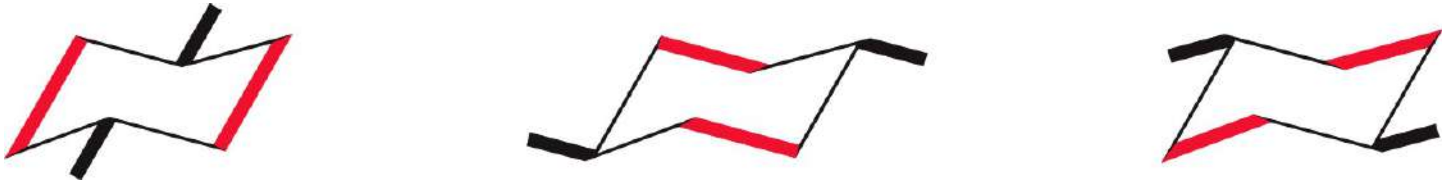
CORRECT



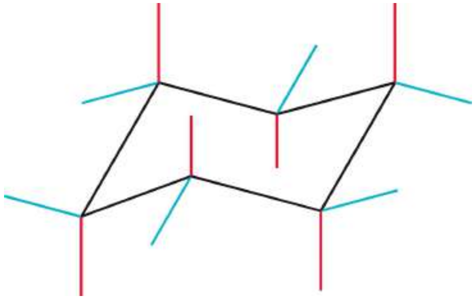
INCORRECT

4.11 Drawing Chairs

- The other SIX atoms attached to a chair are in equatorial positions. Equatorial substituents are positioned at angles parallel to the sets of parallel lines making up the chair itself



- Axial groups shown in red, equatorial groups shown in blue

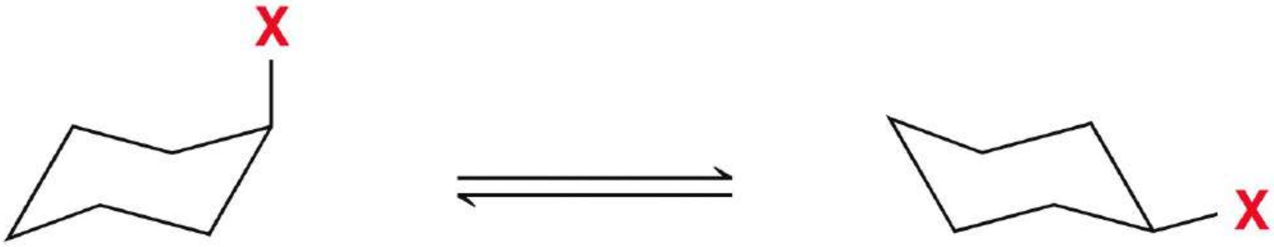


- Practice with SkillBuilders 4.9 and 4.10

4.12 Monosubstituted Cyclohexane

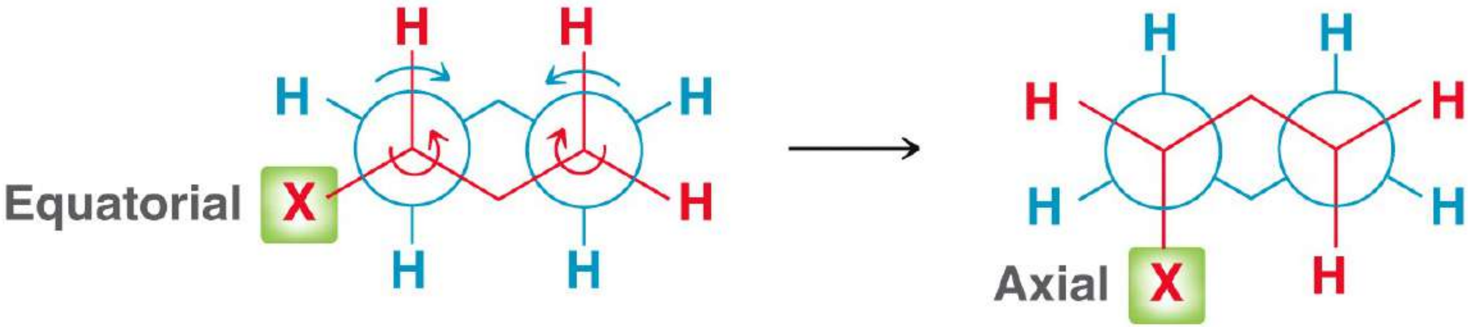
- The vast majority of cyclohexane molecules will exist in the chair conformation at any given moment. WHY?

- When energy (45 kJ/mol) is available, it can flip from one chair form to another. Why is energy needed?



4.12 Monosubstituted Cyclohexane

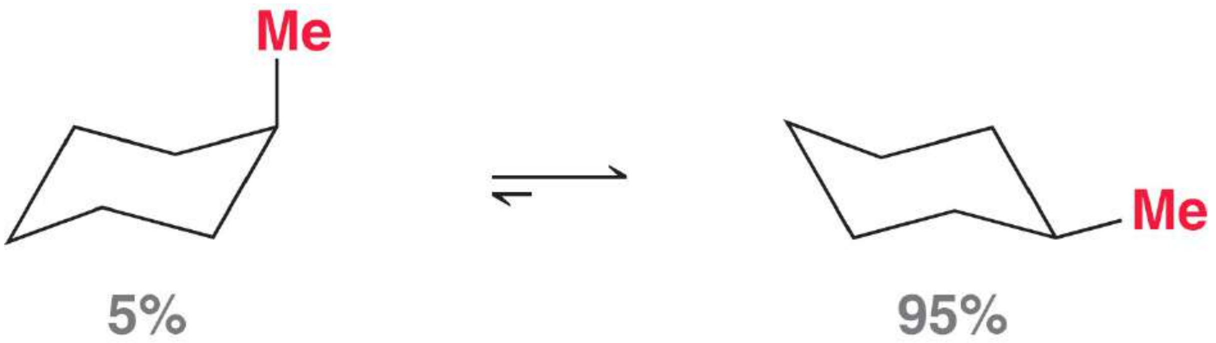
- Flipping a chair is not like flipping a pancake. Flipping a chair is the result of ONLY C-C single bonds rotating.
- The Newman projection below shows how flipping occurs ONLY through rotating bonds and how it will affect the axial or equatorial position of the substituent



- Such flipping is MUCH easier to see with a handheld model. Try it yourself!
- Practice with SkillBuilder 4.11

4.12 Monosubstituted Cyclohexane

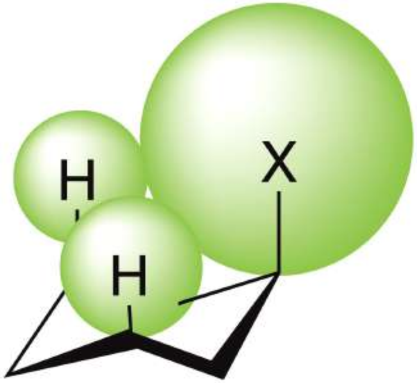
- If both versions of the CHAIR were equally stable, you would have a 50/50 mixture of axial/equatorial
- Consider methylcyclohexane

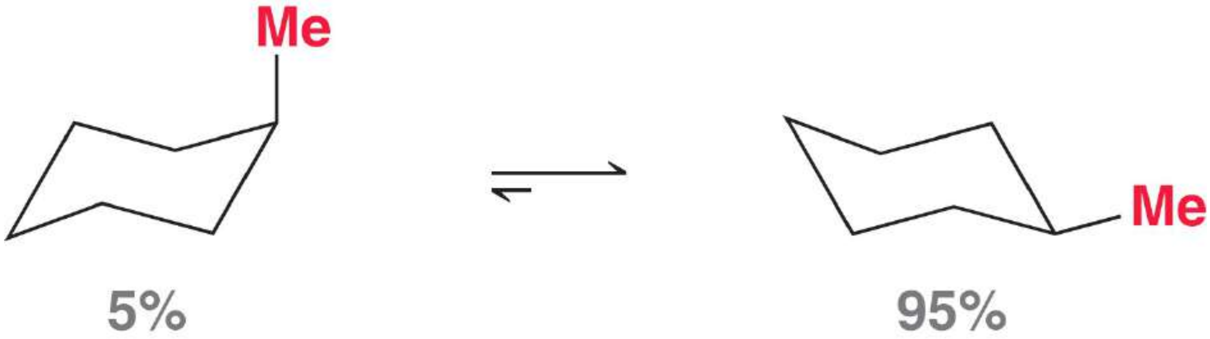


- Why does the equatorial chair dominate the equilibrium?
- Does the axial substituent cause additional angle or torsional strain?

4.12 Monosubstituted Cyclohexane

- The axial substituent causes additional steric strain

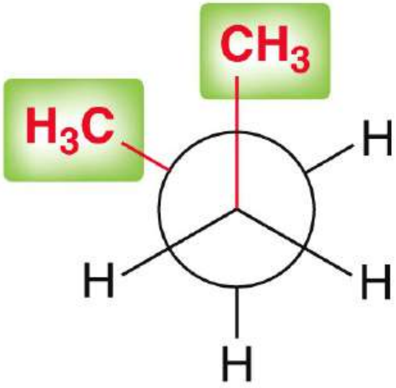




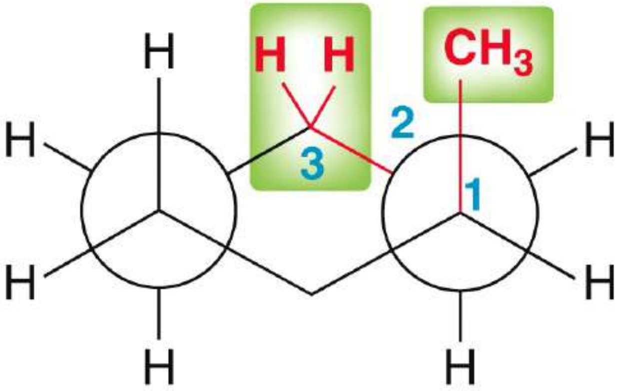
- Such steric crowding is called 1,3-diaxial strain. WHY?

4.12 Monosubstituted Cyclohexane

- 1,3-diaxial interactions are equivalent to gauche interactions

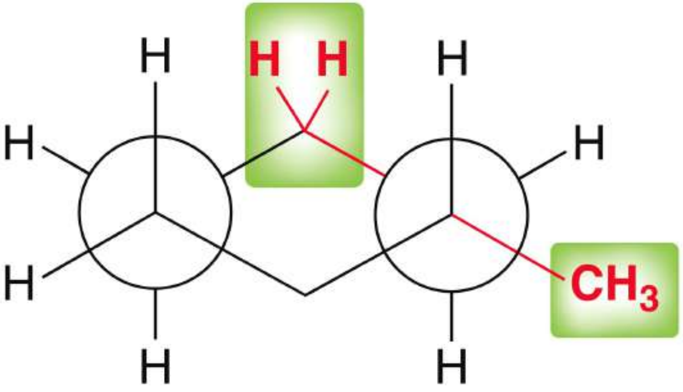


Gauche interaction



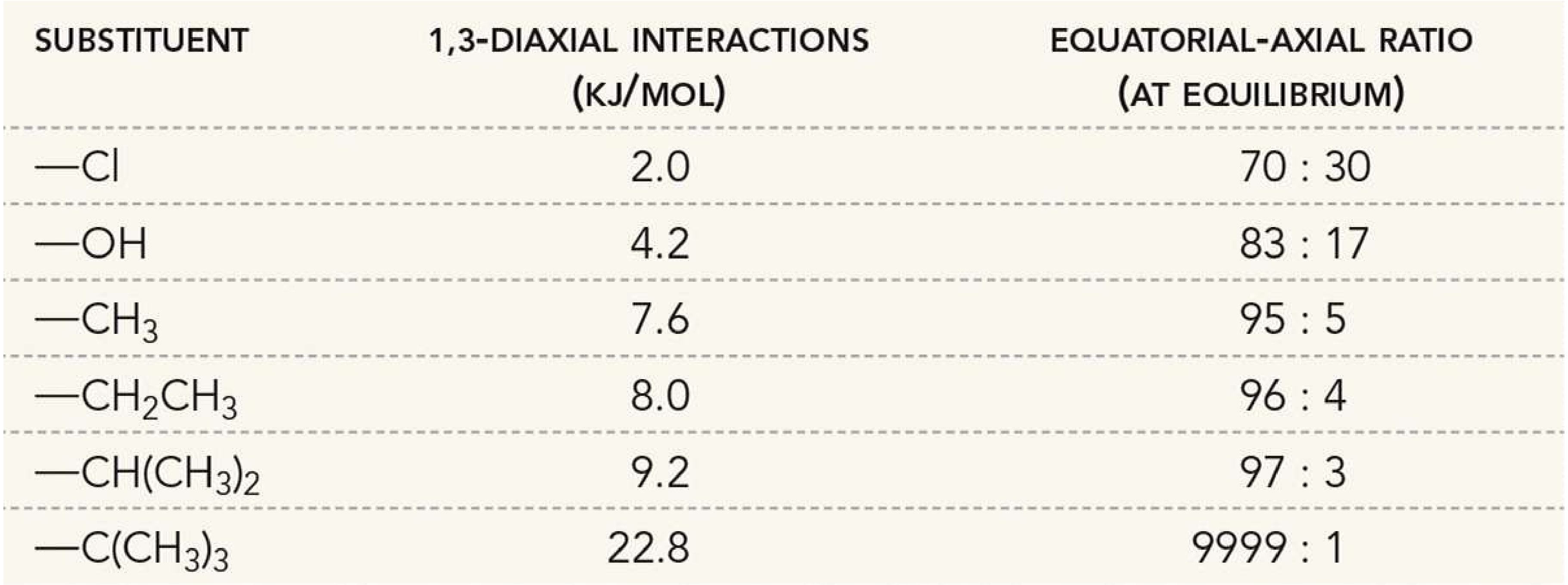
1,3-Diaxial interaction

- When the substituent is in the equatorial position, it is equivalent to an anti interaction



4.12 Monosubstituted Cyclohexane

- Larger groups will cause more steric crowding in the axial position. Consider Table 4.8

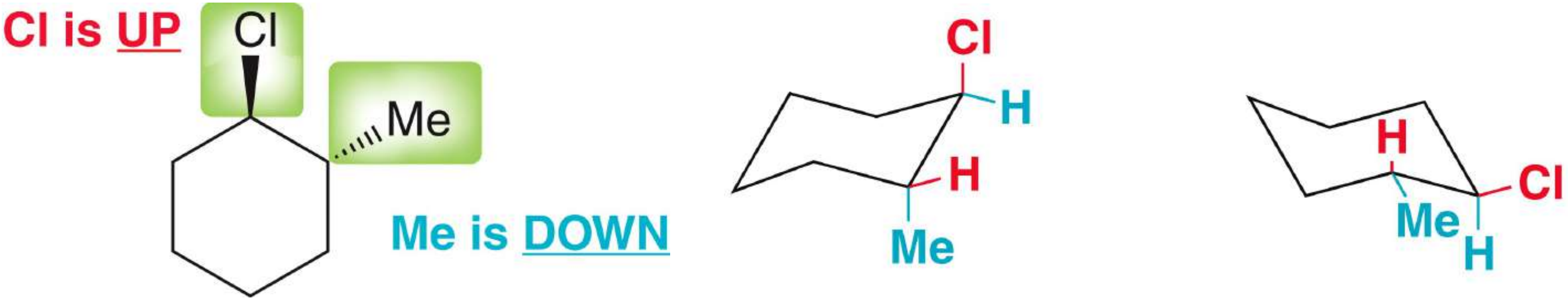


SUBSTITUENT	1,3-DIAXIAL INTERACTIONS (KJ/MOL)	EQUATORIAL-AXIAL RATIO (AT EQUILIBRIUM)
$—Cl$	2.0	70 : 30
$—OH$	4.2	83 : 17
$—CH_3$	7.6	95 : 5
$—CH_2CH_3$	8.0	96 : 4
$—CH(CH_3)_2$	9.2	97 : 3
$—C(CH_3)_3$	22.8	9999 : 1

- Practice with Conceptual Checkpoint 4.30

4.13 Disubstituted Cyclohexane

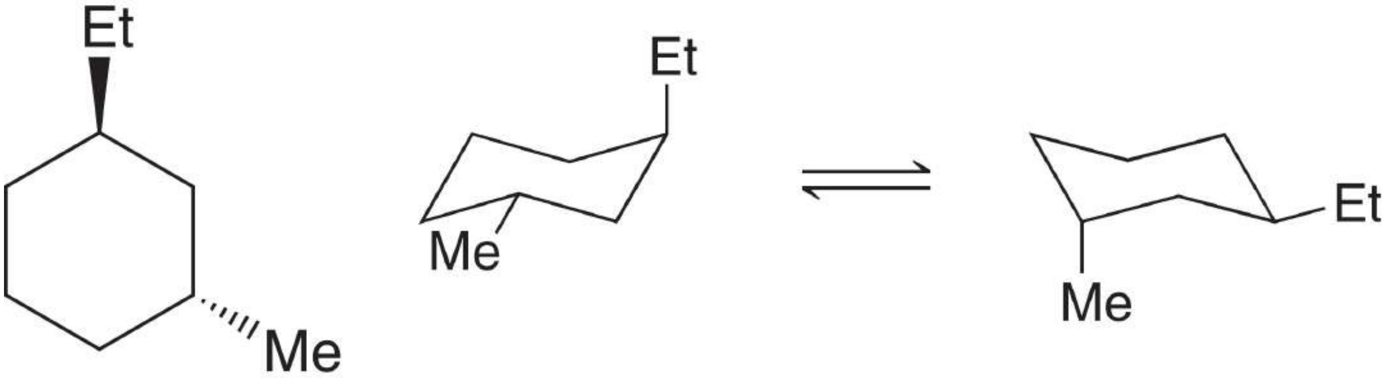
- With multiple substituents, solid or dashed wedges are used to show positioning of the groups or by showing the groups in either axial or equatorial positions



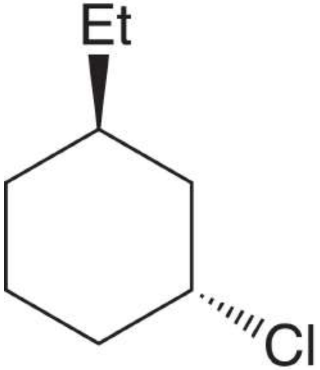
- An UP substituent could be axial or equatorial depending on how the ring is flipped
- Convince yourself that all of the molecules above are identical. It may help to use a handheld model
- Practice with SkillBuilder 4.12

4.13 Disubstituted Cyclohexane

- Consider both chair conformations for the following molecule



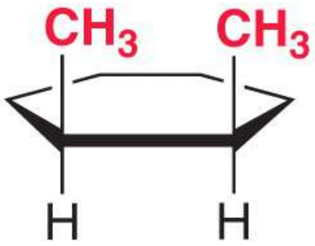
- Which is more stable? WHY?
- Do the same analysis for the following molecule



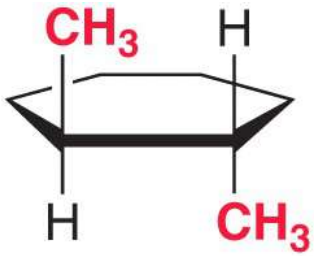
- Practice with SkillBuilder 4.13

4.14 Cis-Trans Isomerism

- When naming a disubstituted cycloalkane, use the prefix *cis* when there are two groups on the same side of the ring
- Use the prefix *trans* when two substituents are on opposite sides of a ring



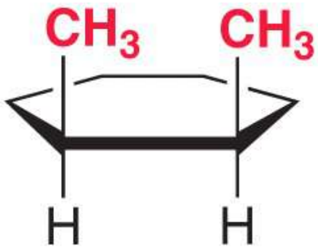
cis-1,2-Dimethylcyclohexane



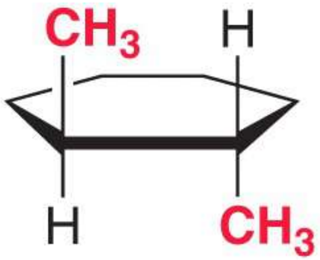
trans-1,2-Dimethylcyclohexane

4.14 Cis-Trans Isomerism

- These two structures are NOT constitutional isomers. WHY?



cis-1,2-Dimethylcyclohexane



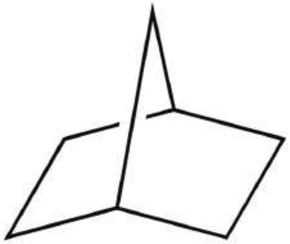
trans-1,2-Dimethylcyclohexane

- They are stereoisomers. HOW?

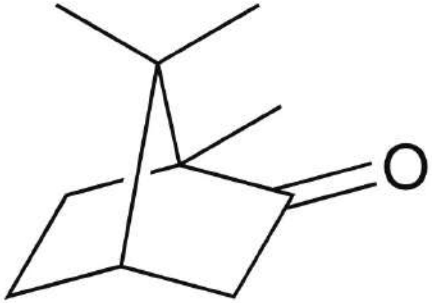
- Practice with conceptual checkpoints 4.36-4.38

4.15 Polycyclic Systems

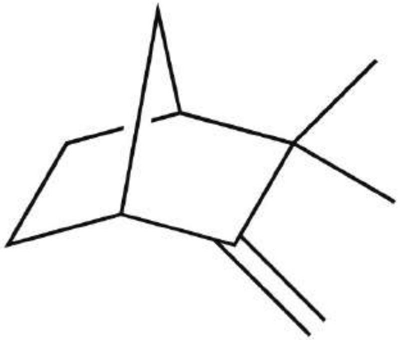
- There are many important structures that result when more than one ring is fused together
- We already looked at bicycloalkanes. Here are a couple more



Bicyclo[2.2.1]heptane (norbornane)



Camphor

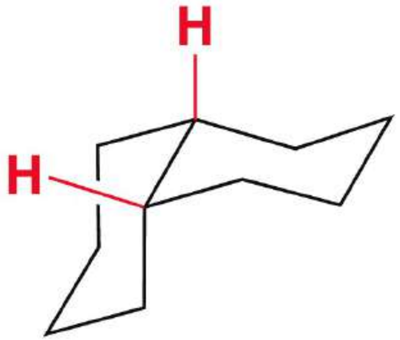


Camphene

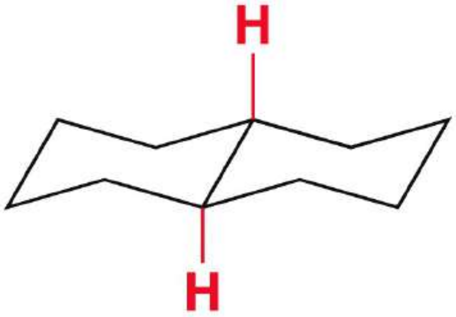
- Camphor and Camphene are fragrant natural products isolated from evergreens

4.15 Polycyclic Systems

- Decalin is formed by fusing two chairs together

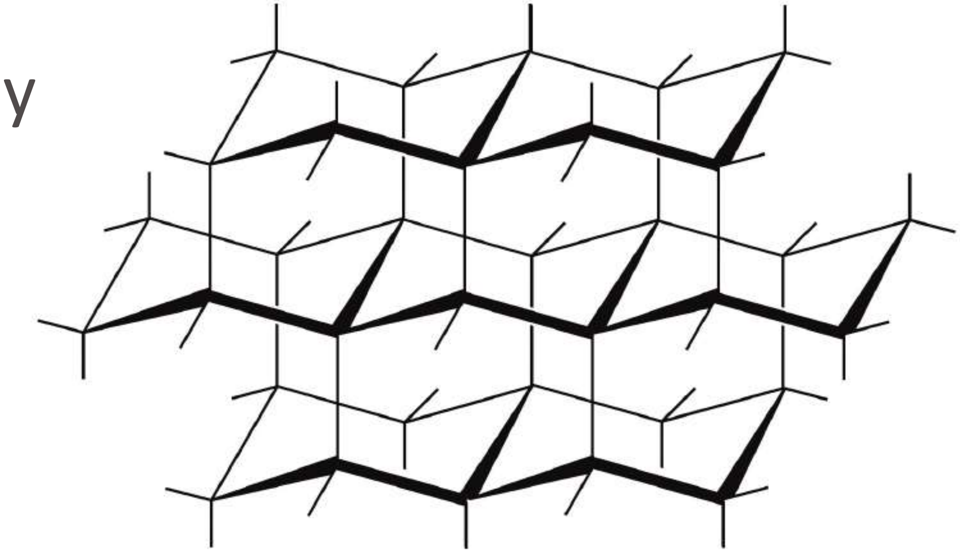


cis-Decalin



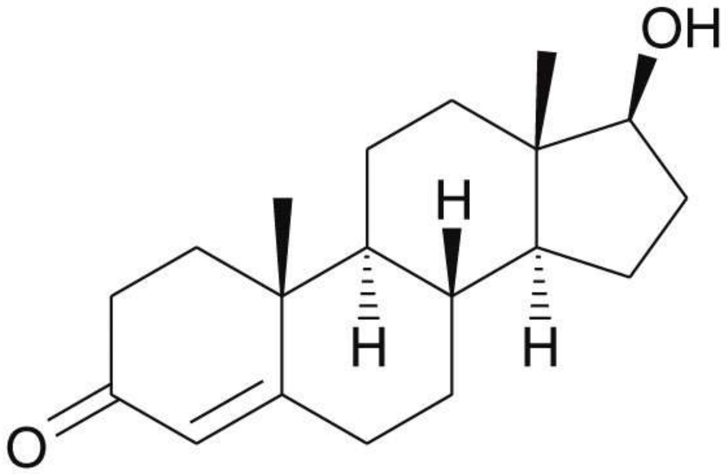
trans-Decalin

- Diamonds are formed by fusing many chairs together three dimensionally in all directions

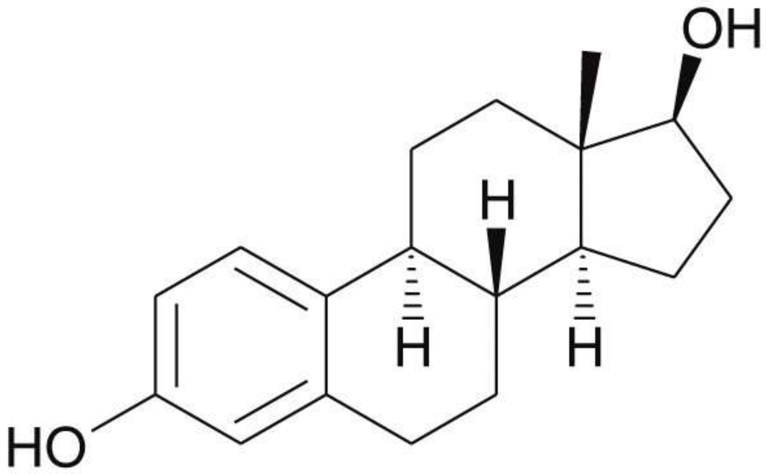


4.15 Polycyclic Systems

- There are many biologically important steroids, all of which involve fusing cycloalkanes as part of their structure



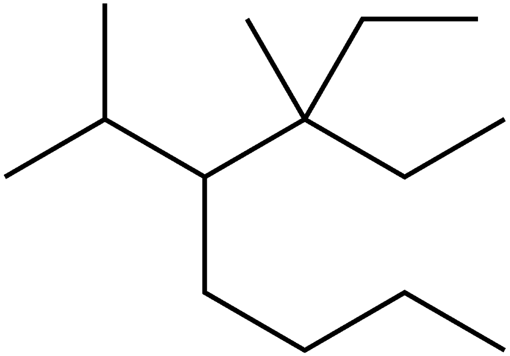
Testosterone



Estradiol

Additional Practice Problems

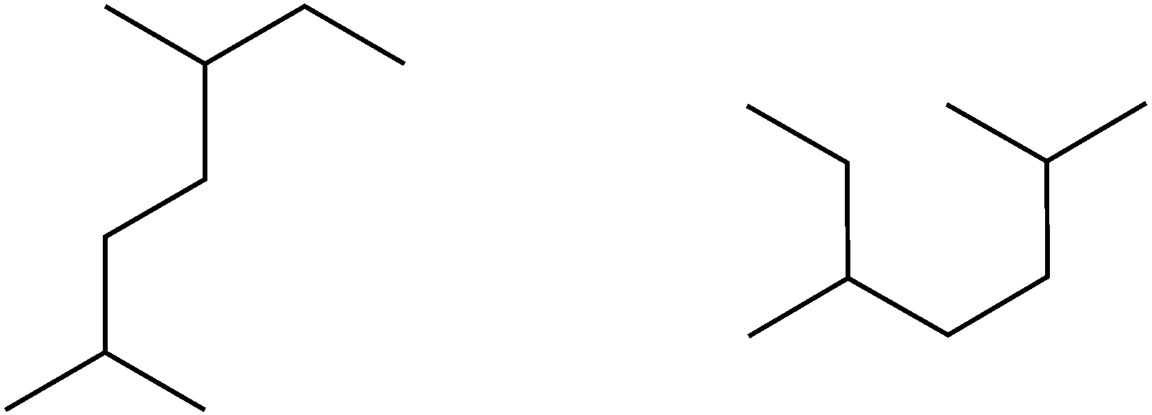
- Name the following molecule



- Draw the bond-line representation for 1,2,6,7-tetrabromo-4-(1,2-dichloroethyl)nonane.

Additional Practice Problems

- Determine whether the following pair are constitutional isomers, identical, or no relationship

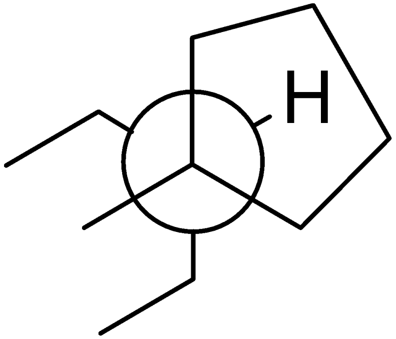


Additional Practice Problems

- Describe how heat of combustion is used to determine the relative stabilities of hydrocarbons with the same formula.

Additional Practice Problems

- Given the following Newman Projection, name the molecule, draw its bond-line structure, and draw a Newman projection showing its highest energy conformation illustrating the torsional strain.



Additional Practice Problems

- Draw the highest and lowest energy chair conformations for the molecule given