Chapter 4
Alkanes and Cycloalkanes

Review of Concepts
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 4. Each of the sentences below appears verbatim in the section entitled Review of Concepts and Vocabulary.

- Hydrocarbons that lack ___________ are called saturated hydrocarbons, or ___________.
- _______________ provide a systematic way for naming compounds.
- Rotation about C-C single bonds allows a compound to adopt a variety of _______________.
- __________ projections are often used to draw the various conformations of a compound.
- ___________ conformations are lower in energy, while ___________ conformations are higher in energy.
- The difference in energy between staggered and eclipsed conformations of ethane is referred to as _____________ strain.
- __________ strain occurs in cycloalkanes when bond angles deviate from the preferred ____°.
- The _______ conformation of cyclohexane has no torsional strain and very little angle strain.
- The term ring flip is used to describe the conversion of one ___________ conformation into the other. When a ring has one substituent…the equilibrium will favor the chair conformation with the substituent in the ___________ position.

Review of Skills
Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 4. The answers appear in the section entitled SkillBuilder Review.

SkillBuilder 4.1 Identifying the Parent

IDENTIFY THE PARENT IN EACH OF THE FOLLOWING COMPOUNDS:

[Diagram of compounds]
SkillBuilder 4.2  Identifying and Naming Substituents

**STEP 1 - IDENTIFY THE PARENT IN THE FOLLOWING COMPOUND**

**STEPS 2 AND 3 - CIRCLE AND NAME ALL ALKYL SUBSTITUENTS CONNECTED TO THE PARENT**

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SkillBuilder 4.3  Identifying and Naming Complex Substituents

**PROVIDE A NAME FOR THE FOLLOWING COMPLEX SUBSTITUENT (HIGHLIGHTED)**

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SkillBuilder 4.4  Assembling the Systematic Name of an Alkane

**PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND**

1) IDENTIFY THE PARENT
2) IDENTIFY AND NAME SUBSTITUENTS
3) ASSIGN LOCANTS TO EACH SUBSTITUENT
4) ALPHABETIZE

---

SkillBuilder 4.5  Assembling the Name of a Bicyclic Compound

**PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND**

1) IDENTIFY THE PARENT
2) IDENTIFY AND NAME SUBSTITUENTS
3) ASSIGN LOCANTS TO EACH SUBSTITUENT
4) ALPHABETIZE

---

SkillBuilder 4.6  Identifying Constitutional Isomers

**DETERMINE IF THESE TWO COMPOUNDS ARE THE SAME BY ASSIGNING A SYSTEMATIC NAME TO EACH AND THEN COMPARING THEM.**

---

SkillBuilder 4.7  Drawing Newman Projections

**STEP 1 - IDENTIFY THE THREE GROUPS CONNECTED TO THE FRONT CARBON ATOM**

**STEP 2 - IDENTIFY THE THREE GROUPS CONNECTED TO THE BACK CARBON ATOM**

**STEP 3 - ASSEMBLE THE NEWMAN PROJECTION FROM THE TWO PIECES OBTAINED IN THE PREVIOUS STEPS**
### SkillBuilder 4.8  Identifying Relative Energy of Conformations

<table>
<thead>
<tr>
<th>STEP 1</th>
<th>STEP 2</th>
<th>STEP 3</th>
</tr>
</thead>
</table>
| DRAW A NEWMAN PROJECTION LOOKING DOWN THE BOND INDICATED<br>

[Diagram of Newman projection]
| DRAW ALL THREE STAGGERED CONFORMATIONS AND DETERMINE WHICH ONE HAS THE FEWEST OR LEAST SEVERE GAUCHE INTERACTIONS<br>

[Three staggered conformations]
| DRAW ALL THREE ECLIPSED CONFORMATIONS AND DETERMINE WHICH ONE HAS THE HIGHEST ENERGY INTERACTIONS<br>

[Three eclipsed conformations]

### SkillBuilder 4.9  Drawing a Chair Conformation

| DRAW A CHAIR CONFORMATION<br>

[Diagram of chair conformation]

### SkillBuilder 4.10  Drawing Axial and Equatorial Positions

| DRAW A CHAIR CONFORMATION SHOWING ALL SIX AXIAL POSITIONS AND ALL SIX EQUATORIAL POSITIONS<br>

[Diagram showing all axial and equatorial positions]

### SkillBuilder 4.11  Drawing Both Chair Conformations of a Monosubstituted Cyclohexane

| DRAW BOTH CHAIR CONFORMATIONS OF BROMOCYCLOHEXANE<br>

[Diagram showing two chair conformations]

### SkillBuilder 4.12  Drawing Both Chair Conformations of Disubstituted Cyclohexanes

| DRAW BOTH CHAIR CONFORMATIONS OF THE FOLLOWING COMPOUND<br>

[Diagram showing two chair conformations]

### SkillBuilder 4.13  Drawing the More Stable Chair Conformation of Polysubstituted Cyclohexanes

| DRAW BOTH CHAIR CONFORMATIONS OF THE FOLLOWING COMPOUND AND DETERMINE WHICH ONE IS MORE STABLE<br>

[Diagram showing two chair conformations and an arrow indicating stability]

Et

Me

Et

Cl

Me

Et

Me

Et
Solutions

4.1.

a) parent = hexane  
b) parent = heptane  
c) parent = heptane  
d) parent = nonane  
e) parent = octane  
f) parent = heptane  
g) parent = cyclopentane  
h) parent = cycloheptene  
i) parent = cyclopropane

4.2.

4.3.

4.4. Only three of the isomers will have a parent name of heptane:

4.5.

a) All groups are methyl groups  
b) methyl  
c) methyl ethyl  
d) methyl
4.6.

a)

b)

4.7.

Systematic = (1,1-dimethylethyl)  
Common = tert-butyl

a)

Systematic = (1-methylethyl)  
Common = isopropyl

b)

Systematic = methyl  
Common = methyl

c)

Systematic = (2,2-dimethylpropyl)  
Common = neopentyl

d)
4.8.

4.9.

4.10.

a) 3,4,6-trimethyloctane
b) sec-butylcyclohexane
c) 3-ethyl-2-methylheptane
d) 3-isopropyl-2,4-dimethylpentane
e) 3-ethyl-2,2-dimethylhexane
f) 2-cyclohexyl-4-ethyl-5,6-dimethyloctane
g) 3-ethyl-2,5-dimethyl-4-propylheptane
h) 5-sec-butyl-4-ethyl-2-methyldecane
i) 2,2,6,6,7,7-hexamethylnonane
j) 4,5-dimethylnonane
k) 2,4,4,6-tetramethylheptane  
l) 2,2,5-trimethylpentane  
m) 4-tert-butylheptane  
n) 3-ethyl-6-isopropyl-2,4-dimethyldecane  
o) 3,5-diethyl-2-methyloctane  
p) 1,3-diisopropylcyclopentane  
q) 3-ethyl-2,5-dimethylheptane

4.11.

\[ \text{a) } \quad \text{b) } \quad \text{c) } \]

4.12.

a) 4-ethyl-1-methylbicyclo[3.2.1]octane  
b) 2,2,5,7-tetramethylbicyclo[4.2.0]octane  
c) 2,7,7-trimethylbicyclo[4.2.2]decane  
d) 3-sec-butyl-2-methylbicyclo[3.1.0]hexane  
e) 2,2-dimethylbicyclo[2.2.2]octane  
f) 2,7-dimethylbicyclo[3.3.0]octane  
g) bicyclo[1.1.0]butane  
h) 5,5-dimethylbicyclo[2.1.1]hexane  
i) 3-(3-methylbutyl)bicyclo[4.4.0]decane

4.13.

\[ \text{a) } \quad \text{b) } \quad \text{c) } \]


a) same compound  
b) same compound  
c) same compound  
d) constitutional isomers

4.15.
4.16.

a) 

b) 

c) 

d) 

e) 

4.17.

a) 

b) 

c) 

4.18. The compounds are not constitutional isomers. They are just two different representations of the same compound. They are both 2,3-dimethylbutane.

4.19.

a) The energy barrier is expected to be approximately 18 kJ / mol (calculation below):

b) The energy barrier is expected to be approximately 16 kJ / mol (calculation below):

4.20.

a) Lowest Energy  Highest Energy 

b) Lowest Energy  Highest Energy 

c) Lowest Energy  Highest Energy 

d) Lowest Energy  Highest Energy
4.21. The gauche conformations are capable of intramolecular hydrogen bonding, as shown below. The anti conformation lacks this stabilizing effect.

\[
\begin{align*}
\text{Anti} & \quad \text{Gauche} & \quad \text{Gauche} \\
\end{align*}
\]

4.22.

4.23.

a)  

b) 

4.24.

4.25.


4.27. There are eight hydrogen atoms in axial positions and seven hydrogen atoms in equatorial positions.

4.28.

a) 

b)
4.29.  

a) The bromine atom occupies an equatorial position.

\[ \text{b) } \quad \text{c) } \]

4.30. Although the OH group is in an axial position, nevertheless, this conformation is capable of intramolecular hydrogen bonding, which is a stabilizing effect:

\[ \quad \]

4.31.  

a)  

\[ \quad \]

b)  

\[ \quad \]
4.34. The two chair conformations of lindane are degenerate. There is no difference in energy between them.

4.35. trans-1,4-di-tert-butylcyclohexane exists predominantly in a chair conformation, because both substituents can occupy equatorial positions. In contrast, cis-1,4-di-tert-butylcyclohexane cannot have both of its substituents in equatorial positions. Each chair conformation has one of the substituents in an axial position, which is too high in energy. The compound can achieve a lower energy state by adopting a twist boat conformation.

4.36. cis-1,3-dimethylcyclohexane is expected to be more stable than trans-1,3-dimethylcyclohexane because the former can adopt a chair conformation in which both substituents are in equatorial positions (highlighted below):

4.37. trans-1,4-dimethylcyclohexane is expected to be more stable than cis-1,4-dimethylcyclohexane because the latter can adopt a chair conformation in which both substituents are in equatorial positions (highlighted below):
4.38. *cis*-1,3-di-tert-butylcyclohexane can adopt a chair conformation in which both tert-butyl groups occupy equatorial positions (highlighted below), and as a result, it is expected to exist primarily in that conformation. In contrast, *trans*-1,3-di-tert-butylcyclohexane cannot adopt a chair conformation in which both tert-butyl groups occupy equatorial positions. In either chair conformation, one of the tert-butyl groups occupies an axial position. This compound can achieve a lower energy state by adopting a twist-boat conformation.

![cis-1,3-di-tert-butylcyclohexane](image1)

where \( R = \text{tert-butyl group} \)

4.39.

a) parent = octane  
b) parent = nonane  
c) parent = octane  
d) parent = heptane

4.40.

a)

![methyl ethyl](image2)

b) isopropyl or (1-methylethyl)

c)

![methyl propyl](image3)

d) tert-butyl or (1,1-dimethylethyl)
4.41.  
   a) 2,3,5-trimethyl-4-propylheptane  
   b) 1,2,4,5-tetramethyl-3-propylcyclohexane  
   c) 2,3,5,9-tetramethylbicyclo[4.4.0]decane  
   d) 1,4-dimethylbicyclo[2.2.2]octane  

4.42.  
   a) same compound  
   b) constitutional isomers  
   c) same compound  

4.43.  

4.44.  

4.45.  
   a)  
   b)  
   c)  

4.46. The energy diagram more closely resembles the shape of the energy diagram for the conformational analysis of ethane.
4.47. Two of the staggered conformations are degenerate. The remaining staggered conformation is lower in energy than the other two, as shown below:

![Potential Energy Graph]

4.48.

a) Cl

b) Cl

c) Cl

4.49.

a) has more CH\(_2\) groups.

b) cannot adopt a chair conformation in which both groups occupy equatorial positions.

c) cannot adopt a chair conformation in which both groups occupy equatorial positions.

d) cannot adopt a chair conformation in which both groups occupy equatorial positions.
4.50.

![Energy Potential Diagram]

4.51.

a) hexane
b) methylcyclohexane
c) methylocyclopentane
d) trans-1,2-dimethylocyclopentane

4.52. Each H-H eclipsing interaction is 4 kJ / mol, and there are two of them (for a total of 8 kJ / mol). The remaining energy cost is associated with the Br-H eclipsing interaction: $15 - 8 = 7$ kJ / mol.

4.53.

\[
\begin{align*}
\text{more stable} \\
\text{(all groups are equatorial)}
\end{align*}
\]

4.54.

a) more stable

b) more stable
4.55.  
   a) The second compound can adopt a chair conformation in which all three substituents occupy equatorial positions. Therefore, the second compound is expected to be more stable.
   b) The first compound can adopt a chair conformation in which all three substituents occupy equatorial positions. Therefore, the first compound is expected to be more stable.
   c) The first compound can adopt a chair conformation in which both substituents occupy equatorial positions. Therefore, the first compound is expected to be more stable.
   d) The first compound can adopt a chair conformation in which all four substituents occupy equatorial positions. Therefore, the first compound is expected to be more stable.

4.56.

4.57. All groups are in equatorial positions.

4.58.  

2,2,4,4-tetramethylbutane
All staggered conformations are degenerate, and the same is true for all eclipsed conformations. The energy diagram has a shape that is similar to the energy diagram for the conformational analysis of ethane:
The staggered conformations have six gauche interactions, each of which has an energy cost of 3.8 kJ / mol. Therefore, each staggered conformation has an energy cost of 22.8 kJ / mol. The eclipsed conformations have three methyl-methyl eclipsing interactions, each of which has an energy cost of 11 kJ / mol. Therefore, each eclipsed conformation has an energy cost of 33 kJ / mol. The difference in energy between staggered and eclipsed conformations is therefore expected to be approximately 10.2 kJ / mol.

4.59.

Increasing energy

4.60.

a) This conformation has three gauche interactions, each of which has an energy cost of 3.8 kJ / mol. Therefore, this conformation has a total energy cost of 11.4 kJ / mol associated with torsional strain and steric strain.
b) This conformation has two methyl-H eclipsing interactions, each of which has an energy cost of 6 kJ / mol. In addition, it also has one methyl-methyl eclipsing interaction, which has an energy cost of 11 kJ / mol. Therefore, this conformation has a total energy cost of 23 kJ / mol associated with torsional strain and steric strain.

4.61.

4.62.

a) equatorial  b) equatorial  c) axial
d) equatorial  e) equatorial  f) axial
4.63.

\[\Delta\]

cyclopropane

4.64. As mentioned in Section 4.9, cyclobutene adopts a slightly puckered conformation in order to alleviate some of the torsional strain associated with the eclipsing hydrogen atoms:

In this non-planar conformation, the individual dipole moments of the C-Cl bonds in trans-1,3-dichlorocyclobutane do not fully cancel each other, giving rise to a small molecular dipole moment.

4.65. Cyclohexene cannot adopt a chair conformation because two of the carbon atoms are \(sp^2\) hybridized and trigonal planar. A chair conformation can only be achieved when all six carbon atoms are \(sp^3\) hybridized and tetrahedral (with bond angles of 109.5\(^\circ\)).

4.66.

a) identical compounds  b) constitutional isomers
c) identical compounds  d) constitutional isomers
e) identical compounds  f) stereoisomers
g) stereoisomers  h) stereoisomers
i) constitutional isomers  j) different conformations of the same compound
k) stereoisomers  l) constitutional isomers

4.67.

a) the trans isomer is expected to be more stable, because the cis isomer has a very high energy methyl-methyl eclipsing interaction (11 kJ / mol). See calculation below.

b) We calculate the energy cost associated with all eclipsing interactions in both compounds. Let’s begin with the trans isomer. It has the following eclipsing interactions, below the ring and above the ring, giving a total of 32 kJ / mol:

<table>
<thead>
<tr>
<th>Eclipsing Interactions Below the Ring</th>
<th>Eclipsing Interactions Above the Ring</th>
</tr>
</thead>
</table>
| **H - H eclipsing interaction**  
(4 kJ / mol)  | **CH\(_3\) - H eclipsing interaction**  
(6 kJ / mol) |
| **CH\(_3\) - H eclipsing interaction**  
(6 kJ / mol) | **H - H eclipsing interaction**  
(4 kJ / mol) |
| **CH\(_3\) - H eclipsing interaction**  
(6 kJ / mol) | **CH\(_3\) - H eclipsing interaction**  
(6 kJ / mol) |
Now let’s focus on the \textit{cis} isomer. It has the following eclipsing interactions, below the ring and above the ring, giving a total of 35 kJ / mol:

\begin{center}
\begin{tabular}{|c|c|}
\hline
\textbf{Eclipsing Interactions Below the Ring} & \textbf{Eclipsing Interactions Above the Ring} \\
\hline
H - H eclipsing interaction (4 kJ / mol) & CH$_3$ - H eclipsing interaction (6 kJ / mol) \\
H - H eclipsing interaction (4 kJ / mol) & CH$_3$ - CH$_3$ eclipsing interaction (11 kJ / mol) \\
H - H eclipsing interaction (4 kJ / mol) & CH$_3$ - H eclipsing interaction (6 kJ / mol) \\
\hline
\end{tabular}
\end{center}

The difference between these two isomers is therefore predicted to be (35 kJ / mol) – (32 kJ / mol) = 3 kJ / mol.

\subsection*{4.68.}
With increasing halogen size, the bond length also increases. That is, the C-I bond is longer than the C-Br bond, which is longer than the C-Cl bond. So, although iodine is much larger than the other halogens, the longer bond length helps to accommodate the additional steric bulk. These two factors (increased steric bulk and increased bond length) mostly offset each other.

\subsection*{4.69.}
\begin{itemize}
\item[a)]
\end{itemize}

b) Comparison of these chair conformations requires a comparison of the energy costs associated with all axial substituents (see Table 4.8). The first chair conformation has two axial substituents: an OH group (energy cost = 4.2 kJ / mol) and a Cl group (energy cost = 2.0 kJ / mol), giving a total of 6.2 kJ / mol. The second chair conformation has two axial substituents: an isopropyl group (energy cost = 9.2 kJ / mol) and an ethyl group (energy cost = 8.0 kJ / mol), giving a total of 17.2 kJ / mol. The first chair conformation has a lower energy cost, and is therefore more stable.

c) Using the numbers calculated in part b, the difference in energy between the these two chair conformations is expected to be (17.2 kJ / mol) – (6.2 kJ / mol) = 11 kJ / mol. Using the numbers in Table 4.8, we see that a difference of 9 kJ / mol corresponds with a ratio of 97:3 for the two conformations. In this case, the difference in energy is more
than 9 kJ / mol, so the ratio should be even higher (more than 97%). Therefore, we do expect the compound to spend more than 95% of its time in the more stable chair conformation.

4.70.
a) cis-Decalin has three gauche interactions, while trans-decalin has only two gauche interactions.

b) trans-Decalin is incapable of ring flipping, because a ring flip of one ring would cause its two alkyl substituents (which comprise the second ring) to be too far apart to accommodate the second ring.