Organic Chemistry 9th edition Brown Solutions Manual

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Solution and Answer Guide

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CHAPTER 2: ALKANES AND CYCLOALKANES

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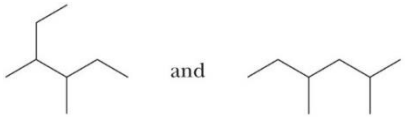
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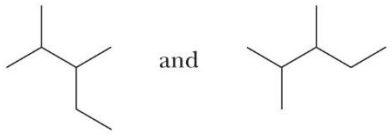
In-Chapter Problems

Constitutional Isomers: Problem 2.1

Do the line-angle formulas in each pair represent the same compound or constitutional isomers?

(a) 

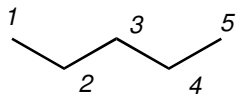
These molecules are constitutional isomers. Each has six carbons in the longest chain. The first has one-carbon branches on carbons 3 and 4 of the chain; the second has one-carbon branches on carbons 2 and 4 of the chain.

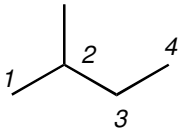
(b) 

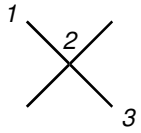
These molecules are identical. Each has five carbons in the longest chain, and one-carbon branches on carbons 2 and 3 of the chain.

Line-Angle Formulas: Problem 2.2

Draw line-angle formulas for the three constitutional isomers with the molecular formula C_5H_{12}.







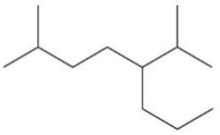
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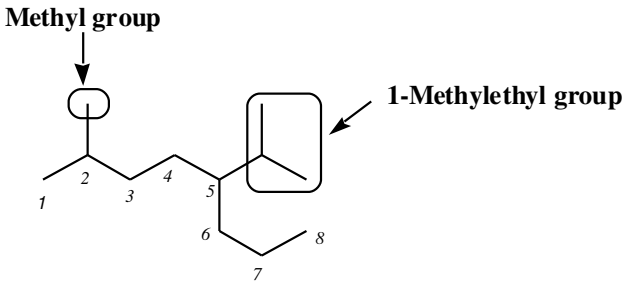
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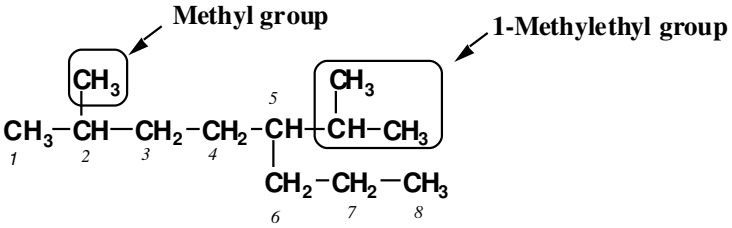
IUPAC Nomenclature I: Problem 2.3

Write IUPAC names for these alkanes.

(a)

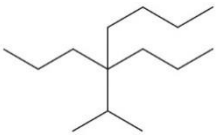


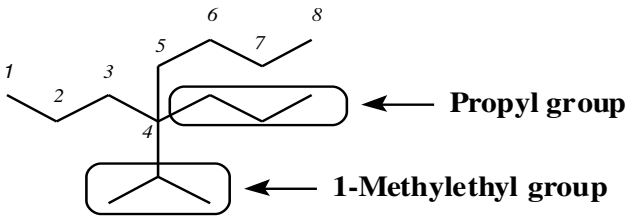


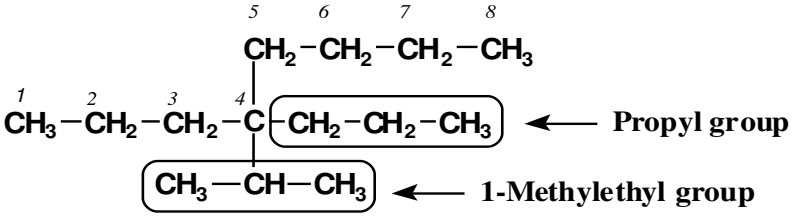


2-Methyl-5-(1-methylethyl)octane

(b)







4-(1-Methylethyl)-4-propyloctane

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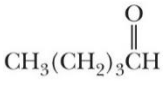
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IUPAC Nomenclature III: Problem 2.4

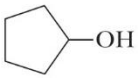
Combine the proper prefix, infix, and suffix and write the IUPAC name for each compound.

(a) 

Propanone

(b) 

Pentanal

(c) 

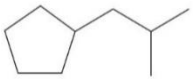
Cyclopentanol

(d) 

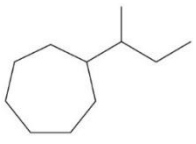
Cycloheptene

IUPAC Nomenclature III: Problem 2.5

Write the molecular formula, IUPAC name, and common name for each cycloalkane.

(a) 

Molecular formula C_9H_{18}
(2-Methylpropyl)cyclopentane (IUPAC)
Isobutylcyclopentane (Common)

(b) 

Molecular formula $C_{11}H_{22}$
(1-Methylpropyl)cycloheptane (IUPAC)
***sec*-Butylcycloheptane (Common)**

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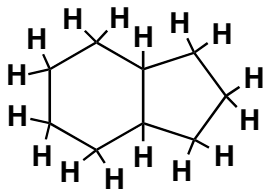
(c) 

Molecular formula C_6H_{12}
1-Ethyl-1-methylcyclopropane (IUPAC and Common)

General Formulas: Problem 2.6

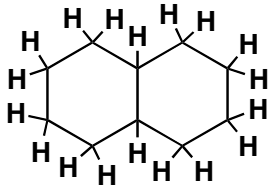
Write molecular formulas for each bicycloalkane, given its number of carbon atoms.

(a) Hydrindane (9 carbons)



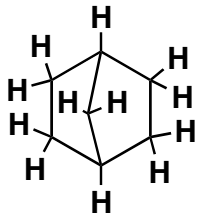
Hydrindane
Molecular formula C_9H_{16}

(b) Decalin (10 carbons)



Decalin
Molecular formula $C_{10}H_{18}$

(c) Norbornane (7 carbons)



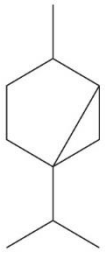
Norbornane
Molecular formula C_7H_{12}

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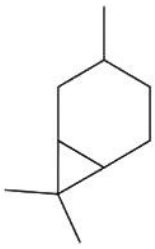
Molecular Formulas: Problem 2.7

Following are the line-angle formulas and names of four bicycloalkanes. Write the molecular formula of each compound. Which of these compounds are constitutional isomers?

(a) 

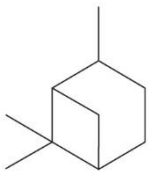
Thujane

Molecular formula: $C_{10}H_{18}$

(b) 

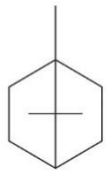
Carane

Molecular formula: $C_{10}H_{18}$

(c) 

Pinane

Molecular formula: $C_{10}H_{18}$

(d) 

Bornane

Molecular formula: $C_{10}H_{18}$

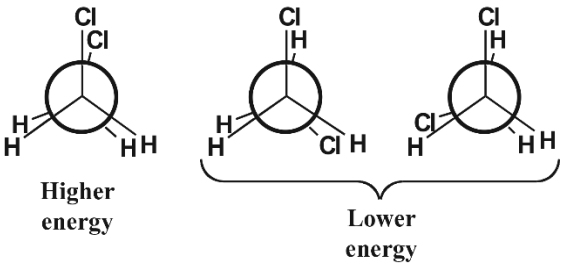
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Newman Projections: Problem 2.8

For 1,2-dichloroethane:

(a) Draw Newman projections for all eclipsed conformations formed by rotation from 0° to 360° about the carbon-carbon single bond.



(b) Which eclipsed conformation(s) has (have) the lowest energy? Which has (have) the highest energy?

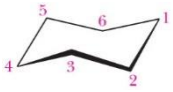
The chlorine atoms are the largest by far. As a result, when the chlorine atoms are eclipsed with each other (structure on the left), their steric interaction causes the higher overall energy.

(c) Which, if any, of these eclipsed conformations are related by reflection?

The two lower energy conformations (structures on the right) are related by reflection as they represent "mirror images" of each other.

Axial Versus Equatorial Groups I: Problem 2.9

Following is a chair conformation of cyclohexane with the carbon atoms numbered 1 through 6.



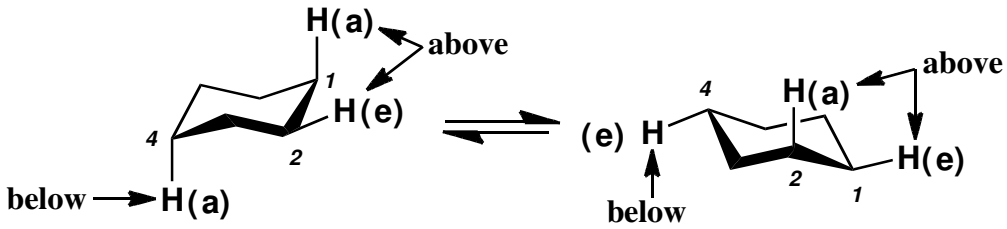
(a) Draw hydrogen atoms that are above the plane of the ring on carbons 1 and 2 and below the plane of the ring on carbon 4.

(b) Which of these hydrogens are equatorial? Which are axial?

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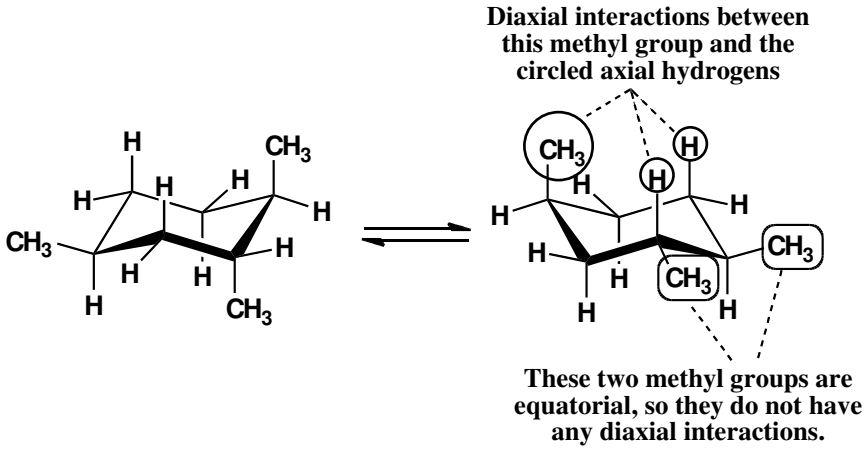
(c) Draw the alternative chair conformation. Which hydrogens are equatorial? Which are axial? Which are above the plane of the ring? Which are below it?

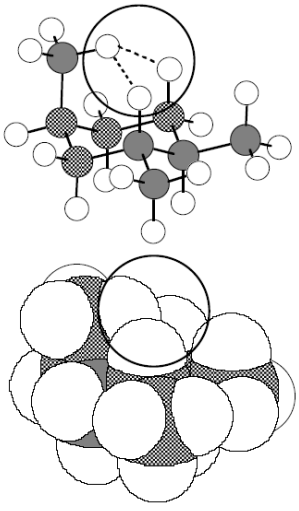


In this figure, (a) = axial and (e) = equatorial.

Axial Versus Equatorial Groups II: Problem 2.10

Draw the alternative chair conformation for the trisubstituted cyclohexane given in Example 2.10. Label all CH_3/H 1,3-diaxial interactions in this chair conformation.





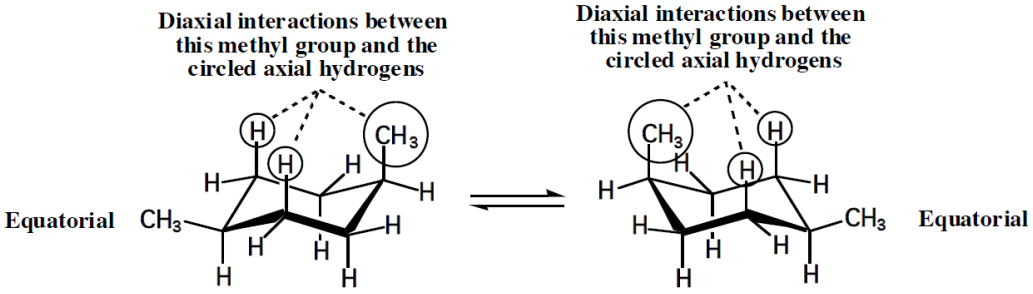
Note how in the preceding equilibrium, the new chair conformation (on the right) is the more stable due to having fewer diaxial interactions (See Problem 2.13).

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Equilibrium Populations of Conformations: Problem 2.11

Draw a chair conformation of 1,4-dimethylcyclohexane in which one methyl group is equatorial and the other is axial. Draw the alternative chair conformation and calculate the ratio of the two conformations at 25°C.



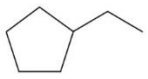
Each chair conformation has diaxial interactions between the circled axial methyl group and circled axial hydrogen atoms. Because each chair has the same number of diaxial interactions, they are of the same energy. The ratio of these two conformations must therefore be 1:1.

Cis Versus *Trans* Isomerism: Problem 2.12

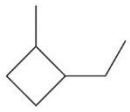
Which cycloalkanes show *cis,trans* isomerism? For each that does, draw both isomers.

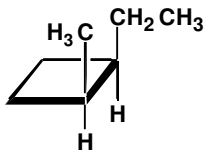
(a) 

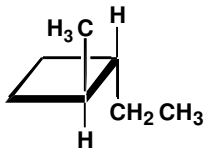
1,3-Dimethylcyclopentane shows *cis,trans* isomerism. Here, the ring is drawn as a planar pentagon with substituents above and below the plane of the pentagon.

(b) 

Ethylcyclopentane does not show *cis,trans* isomerism.

(c) 





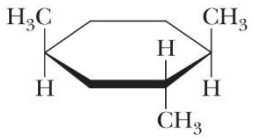
1-Ethyl-2-methylcyclobutane shows *cis,trans* isomerism.

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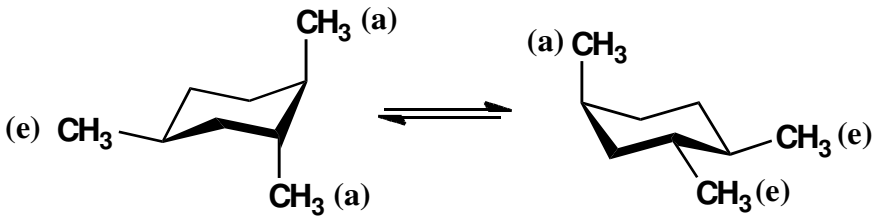
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Cyclohexane Rings: Problem 2.13

Following is a planar hexagon representation for one isomer of 1,2,4-trimethylcyclohexane. Draw the alternative chair conformations of this compound and state which of the two is more stable.



Following are alternative chair conformations for this isomer of 1,2,4-trimethylcyclohexane. The alternative chair conformation on the right is the more stable because it has only one axial methyl group.

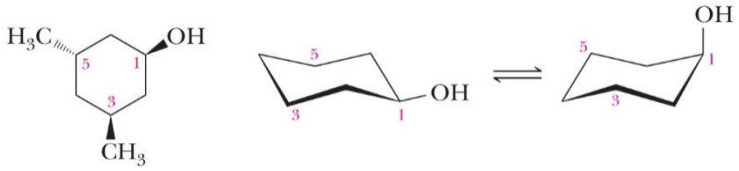


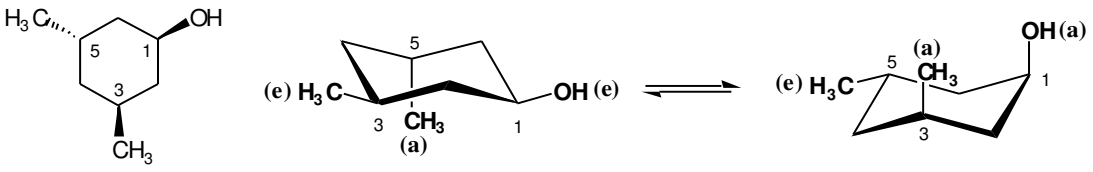
less stable chair (two methyl groups axial)

more stable chair (one methyl group axial, one gauche interaction)

Substituted Cyclohexane Rings: Problem 2.14

Here is one *cis,trans* isomer of 3,5-dimethylcyclohexanol. Complete the alternative chair conformations.



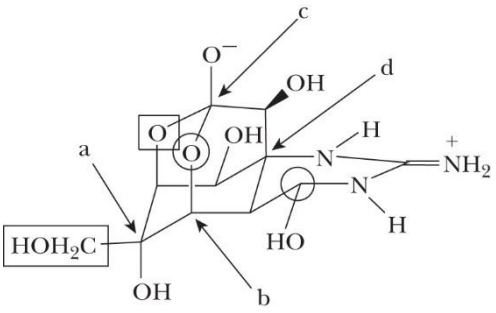


More stable

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MCAT Practice Questions: Tetrodotoxin



Tetrodotoxin

A. What are the relationships between the boxed atoms and the circled atoms?
1. The boxed atoms are *trans*, and the circled atoms are *cis*.

2. The boxed atoms are *cis*, and the circled atoms are *trans*.

3. Both sets of atoms are *cis*.

4. Both sets of atoms are *trans*.

B. To what kinds of carbons, 1°, 2°, 3°, or 4°, do the arrows a, b, c, and d point?
1. They are all tertiary.

2. Carbons a and c are tertiary, while b and d are secondary.

3. Carbon b is secondary, while carbons a, b, and c are tertiary.

4. Carbon c is primary, carbon b is secondary, and carbons a and d are tertiary.

C. What is the hybridization of the nitrogens within the ring on the right and the nitrogen protruding from the ring?
1. The nitrogens within the ring are sp^3, while the protruding nitrogen is sp^2.

2. They are all sp^3.

3. They are all sp^2.

Alkane Boiling Points: Problem 2.15

Arrange the alkanes in each set in order of increasing boiling point.

(a) 2-Methylbutane, 2,2-dimethylpropane, and pentane

2,2-Dimethylpropane (bp 9.5°C) **2-Methylbutane (bp 29°C)** **Pentane (bp 36°C)**

(b) 3,3-Dimethylheptane, 2,2,4-trimethylhexane, and nonane

2,2,4-Trimethylhexane (bp 130°C) **3,3-Dimethylheptane (bp 138°C)** **Nonane (bp 151°C)**

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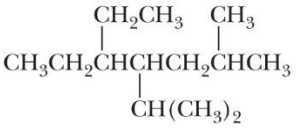
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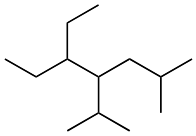
End-of-Chapter Problems

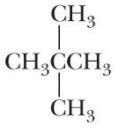
An asterisk (*) indicates an applied problem.

Problem 2.16

Write a line-angle formula for each condensed structural formula.

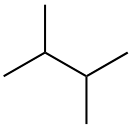
(a) 

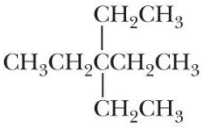


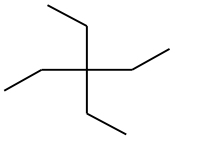
(b) 



(c) $(CH_3)_2CHCH(CH_3)_2$



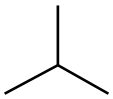
(d) 



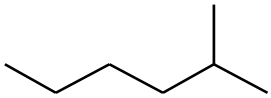
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(e) $(CH_3)_3CH$



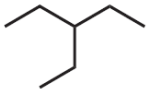
(f) $CH_3(CH_2)_3CH(CH_3)_2$



Problem 2.17

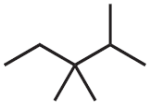
Write the molecular formula of each alkane.

(a)



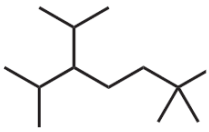
C_7H_{16}

(b)



C_8H_{18}

(c)



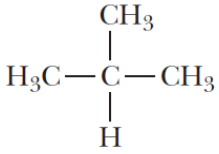
$C_{13}H_{28}$

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Problem 2.18

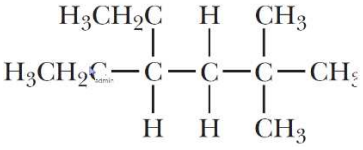
Using parentheses and subscripts, provide an even more abbreviated formula for each structural formula.

(a) 

$CH(CH_3)_3$

(b) $CH_3CH_2CH_2CH_2CH_2CH_3$

$CH_3(CH_2)_4CH_3$

(c) 

$CH(CH_2CH_3)_2CH_2C(CH_3)_3$

Constitutional Isomerism

Problem 2.19

Which statements are true about constitutional isomers?

(a) They have the same molecular formula.

(b) They have the same molecular weight.

(c) They have the same order of attachment of atoms.

(d) They have the same physical properties.

Statements (a) and (b) are true, statements (c) and (d) are false.

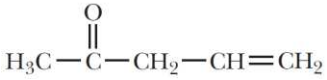
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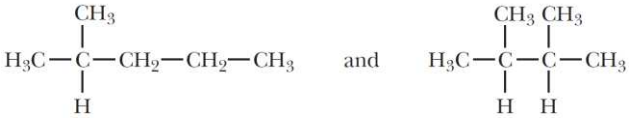
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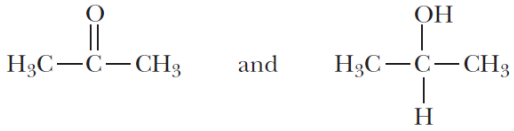
Problem 2.20

Indicate whether the compounds in each set are constitutional isomers.

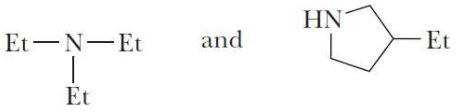
(a)  and $H_3C—CH_2—CH_2—CH_2—CH_2—CH_3$

(b)  and $H_3C—CH_2—C{\equiv}C—CH_2—OH$

(c) 

(d) 

(e)  and $CH_3—CH_2—CH{=}CH—CH_2—CH_3$

(f) 

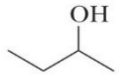
Sets (b), (c), and (e) are constitutional isomers; sets (a), (d), and (f) are not.

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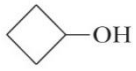
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Problem 2.21

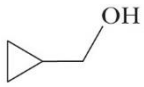
Each member of the following set of compounds is an alcohol; that is, each contains an —OH (hydroxyl group, Section 1.3A). Which line-angle formulas represent the same compound? Which represent constitutional isomers?

(a) 

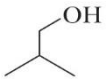
$C_4H_{10}O$

(b) 

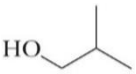
C_4C_8O

(c) 

C_4H_8O

(d) 

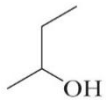
$C_4H_{10}O$

(e) 

$C_4H_{10}O$

(f) 

$C_4H_{10}O$

(g) 

$C_4H_{10}O$

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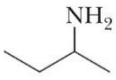
(h) 

$C_7H_{14}O$

Structural formulas (d) and (e) are the same structural formula, and structural formulas (a) and (g) are also the same structural formula. Constitutional isomers have the same molecular formula but different connectivities between atoms. Structural formulas (a)/(g), (d)/(e), and (f) are constitutional isomers. Structural formulas (b) and (c) represent another set of constitutional isomers.

Problem 2.22

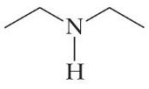
Each of the following compounds is an amine (Section 1.3B). Which line-angle formulas represent the same compound? Which represent constitutional isomers?

(a) 

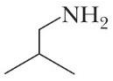
$C_4H_{11}N$

(b) 

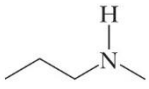
C_4H_9N

(c) 

$C_4H_{11}N$

(d) 

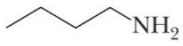
$C_4H_{11}N$

(e) 

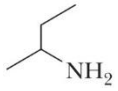
$C_4H_{11}N$

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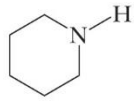
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(f) 

$C_4H_{11}N$

(g) 

$C_4H_{11}N$

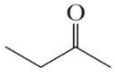
(h) 

$C_5H_{11}N$

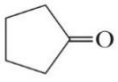
Structural formulas (a) and (g) represent the same structural formula. Constitutional isomers have the same molecular formula but different connectivities between atoms. Structural formulas (a)/(g), (c), (d), (e), and (f) are constitutional isomers.

Problem 2.23

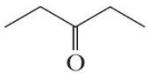
Each of the following compounds is either an aldehyde or a ketone (Section 1.3C). Which line-angle formulas represent the same compound? Which represent constitutional isomers?

(a) 

C_4H_8O

(b) 

C_5H_8O

(c) 

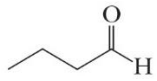
$C_5H_{10}O$

(d) 

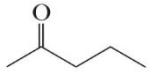
C_4H_8O

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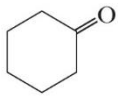
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(e) 

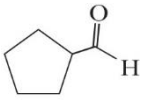
C_4H_8O

(f) 

$C_5H_{10}O$

(g) 

$C_6H_{10}O$

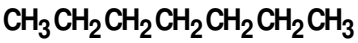
(h) 

$C_6H_{10}O$

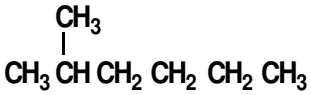
All of these molecules are different. Constitutional isomers have the same molecular formula but different connectivities between atoms. Compounds (a), (d), and (e) are constitutional isomers. Compounds (c) and (f) represent another set of constitutional isomers. The third set of constitutional isomers is composed of (g) and (h).

Problem 2.24

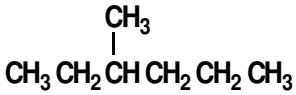
Draw structural formulas and write IUPAC names for the nine constitutional isomers with the molecular formula C_7H_{16}.



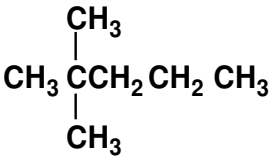
Heptane
(bp 94.8°C)



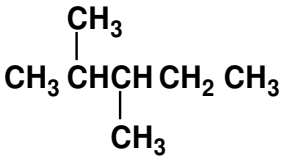
2-Methylhexane
(bp 90.0°C)



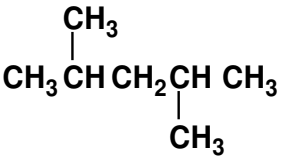
3-Methylhexane
(bp 92.0°C)



2,2-Dimethylpentane
(bp 79.2°C)



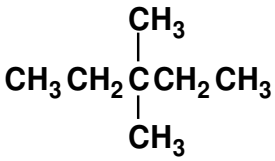
2,3-Dimethylpentane
(bp 89.8°C)



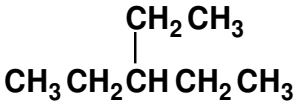
2,4-Dimethylpentane
(bp 80.5°C)

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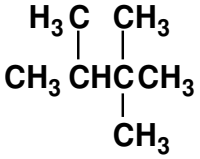
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3,3-Dimethylpentane
(bp 86.1°C)



3-Ethylpentane
(bp 93.5°C)

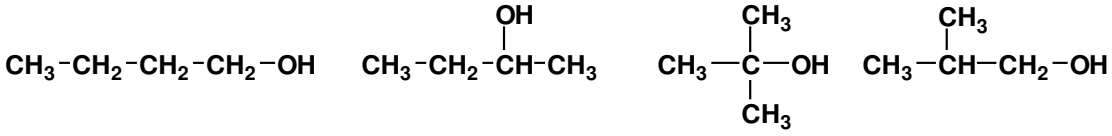


2,2,3-Trimethylbutane
(bp 80.9°C)

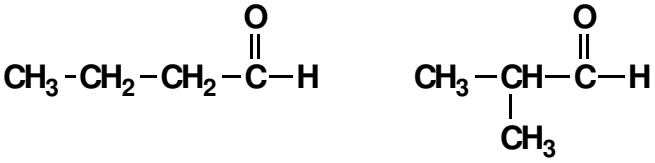
Problem 2.25

Draw structural formulas for all of the following.

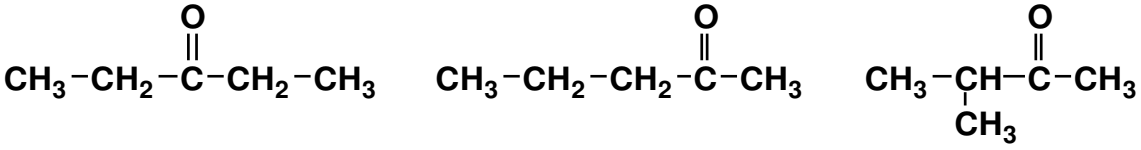
(a) Alcohols with the molecular formula $C_4H_{10}O$



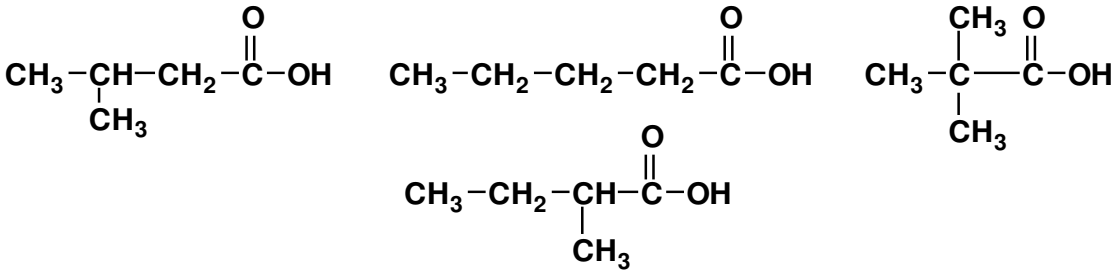
(b) Aldehydes with the molecular formula C_4H_8O



(c) Ketones with the molecular formula $C_5H_{10}O$



(d) Carboxylic acids with the molecular formula $C_5H_{10}O_2$



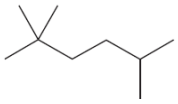
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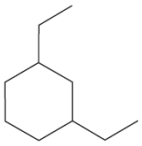
Nomenclature of Alkanes and Cycloalkanes

Problem 2.26

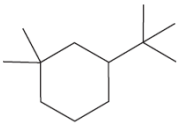
Write IUPAC names for these alkanes and cycloalkanes.

(a) 

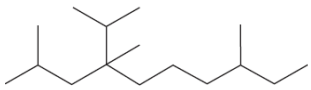
2,2,5-Trimethylhexane

(b) 

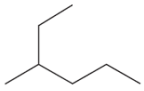
1,3-Diethylcyclohexane

(c) 

1,1-Dimethyl-3-(1,1-dimethylethyl)-cyclohexane

(d) 

2,4,8-Trimethyl-4-(1-methylethyl)decane

(e) 

3-Methylhexane

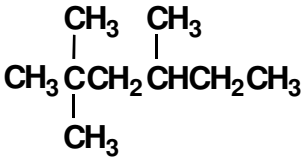
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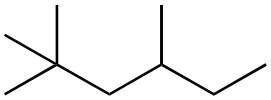
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Problem 2.27

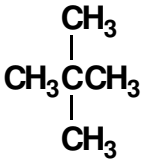
Write structural formulas and line-angle formulas for the following alkanes and cycloalkanes.

(a) 2,2,4-Trimethylhexane



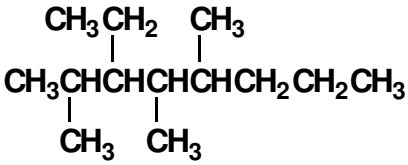


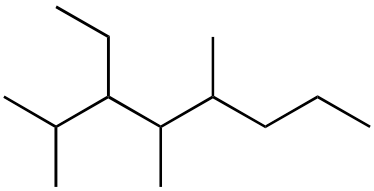
(b) 2,2-Dimethylpropane



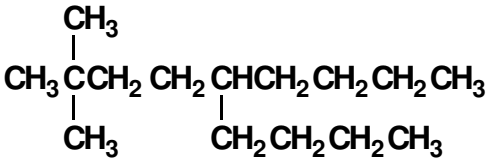


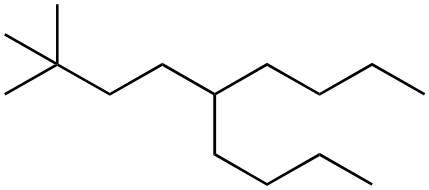
(c) 3-Ethyl-2,4,5-trimethyloctane



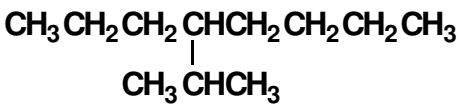


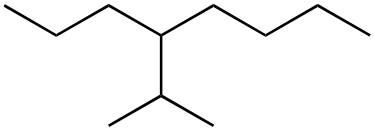
(d) 5-Butyl-2,2-dimethylnonane





(e) 4-(1-Methylethyl)octane

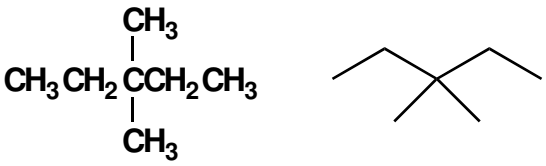




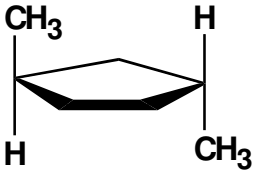
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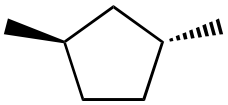
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(f) 3,3-Dimethylpentane

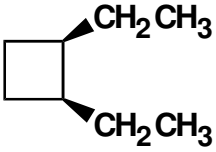


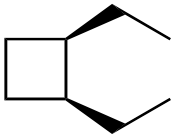
(g) *trans*-1,3-Dimethylcyclopentane





(h) *cis*-1,2-Diethylcyclobutane

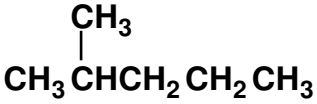




Problem 2.28

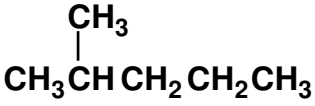
Explain why each is an incorrect IUPAC name and write the correct IUPAC name for the intended compound.

(a) 1,3-Dimethylbutane



The longest chain is pentane.
Its IUPAC name is 2-methylpentane.

(b) 4-Methylpentane

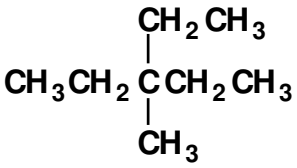


The pentane is numbered incorrectly.
Its IUPAC name is 2-methylpentane.

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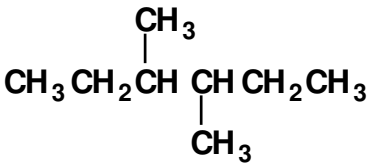
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(c) 2,2-Diethylbutane



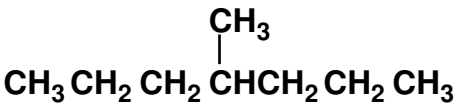
The longest chain is pentane.
Its IUPAC name is 3-ethyl-3-methylpentane.

(d) 2-Ethyl-3-methylpentane



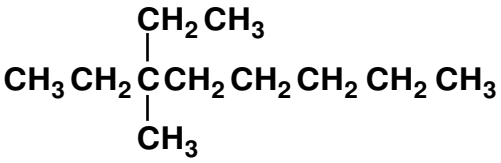
The longest chain is hexane.
Its IUPAC name is 3,4-dimethylhexane.

(e) 2-Propylpentane



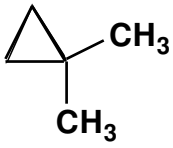
The longest chain is heptane.
Its IUPAC name is 4-methylheptane.

(f) 2,2-Diethylheptane



The longest chain is octane.
Its IUPAC name is 3-ethyl-3-methyloctane.

(g) 2,2-Dimethylcyclopropane

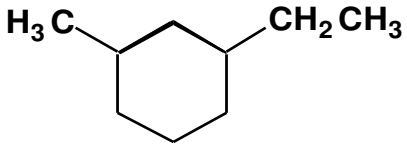


The ring is numbered incorrectly.
Its IUPAC name is 1,1-dimethylcyclopropane.

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(h) 1-Ethyl-5-methylcyclohexane

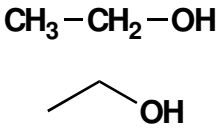


The ring is numbered incorrectly.
Its IUPAC name is 1-ethyl-3-methylcyclohexane.

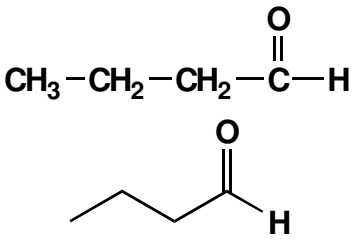
Problem 2.29

For each IUPAC name, draw the corresponding structural formula and line-angle formula.

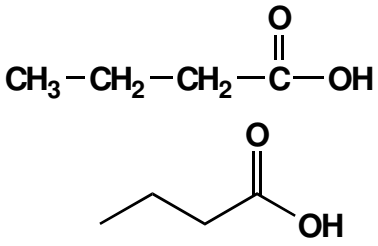
(a) Ethanol



(b) Butanal



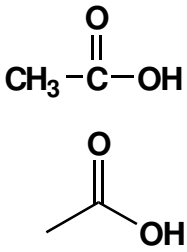
(c) Butanoic acid



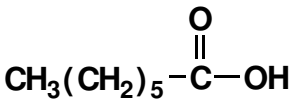
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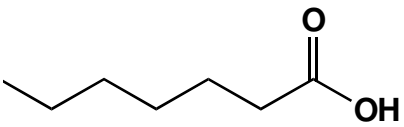
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(d) Ethanoic acid

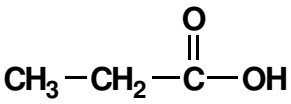


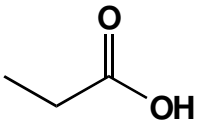
(e) Heptanoic acid



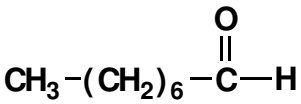


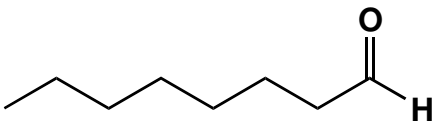
(f) Propanoic acid





(g) Octanal

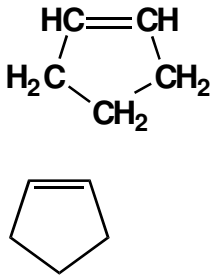




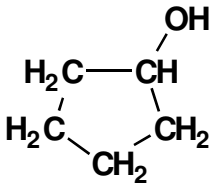
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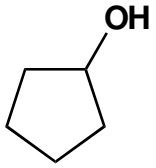
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(h) Cyclopentene

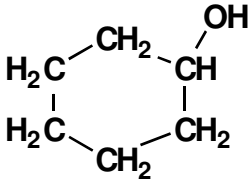


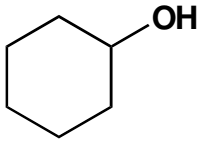
(i) Cyclopentanol





(j) Cyclopentanone

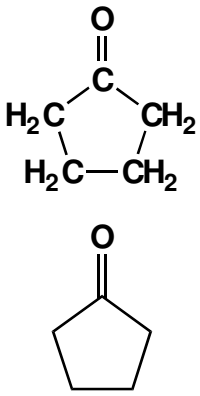




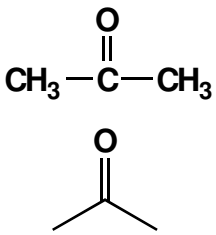
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(k) Cyclohexanol

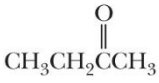


(l) Propanone



Problem 2.30

Write the IUPAC name for each compound.

(a) 

Butanone

(b) 

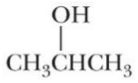
Propanal

(c) 

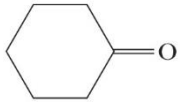
Hexanoic acid

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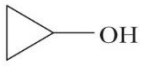
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(d) 

2-Propanol

(e) 

Cyclohexanone

(f) 

Cyclopropanol

(g) $CH_3CH{=}CH_2$

Propene

(h) 

Cyclohexene

Problem 2.31

Assume for the purposes of this problem that to be an alcohol (-ol) or an amine (-amine), the hydroxyl or amino group must be bonded to a tetrahedral (sp^3 hybridized) carbon atom. Write the structural formula of a compound with an unbranched chain of four carbon atoms that is an:

The IUPAC names are only provided for your reference. You do not yet know how to name all of these.

(a) Alkane

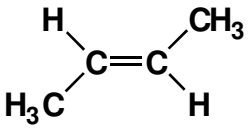
$$CH_3-CH_2-CH_2-CH_3$$

Butane

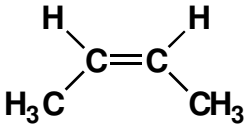
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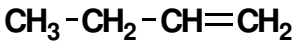
(b) Alkene



***trans*-2-Butene**

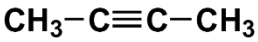


***cis*-2-Butene**

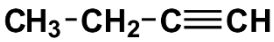


1-Butene

(c) Alkyne

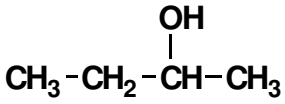


2-Butyne



1-Butyne

(d) Alkanol



2-Butanol

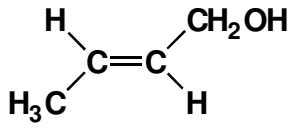


1-Butanol

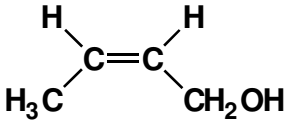
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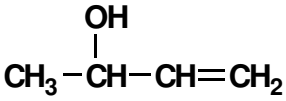
(e) Alkenol



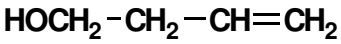
***trans*-2-Buten-1-ol**



***cis*-2-Buten-1-ol**

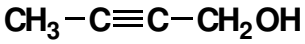


3-Buten-2-ol

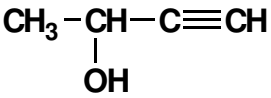


3-Buten-1-ol

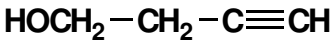
(f) Alkynol



2-Butyn-1-ol



3-Butyn-2-ol

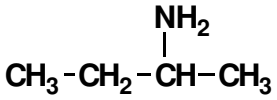


3-Butyn-1-ol

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(g) Alkanamine



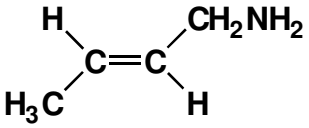
2-Butanamine



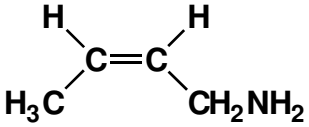
1-Butanamine

Note: You will learn later why the OH group cannot be bonded directly to a double bond or a triple bond.

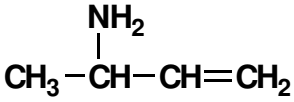
(h) Alkenamine



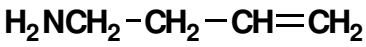
***trans*-2-Buten-1-amine**



***cis*-2-Buten-1-amine**



3-Buten-2-amine

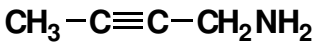


3-Buten-1-amine

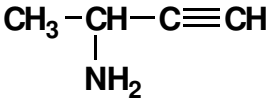
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(i) Alkynamine



2-Butyn-1-amine



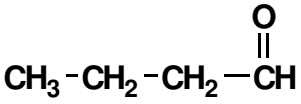
3-Butyn-2-amine



3-Butyn-1-amine

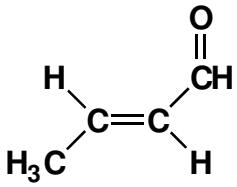
Note: You will learn later why the NH_2 group cannot be attached directly to a double bond or a triple bond.

(j) Alkanal

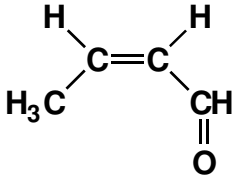


Butanal

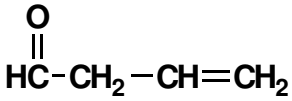
(k) Alkenal



***trans*-2-Butenal**



***cis*-2-Butenal**

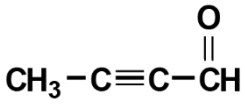


3-Butenal

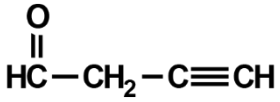
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(l) Alkynal

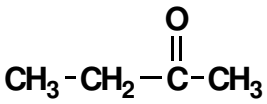


2-Butynal



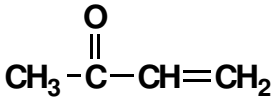
3-Butynal

(m) Alkanone



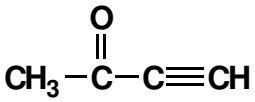
Butanone

(n) Alkenone



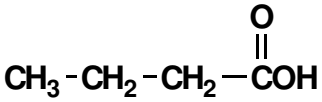
3-Butenone

(o) Alkynone



3-Butynone

(p) Alkanoic acid

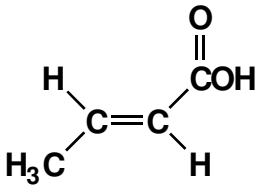


Butanoic acid

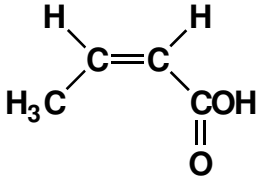
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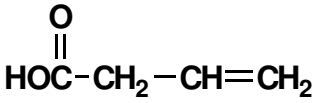
(q) Alkenoic acid



***trans*-2-Butenoic acid**

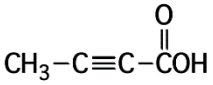


***cis*-2-Butenoic acid**

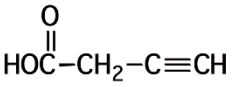


3-Butenoic acid

(r) Alkynoic acid



2-Butynoic acid



3-Butynoic acid

(*Note:* Only one structural formula is possible for some parts of this problem. For other parts, two or more structural formulas are possible. Where two or more are possible, we will deal with how the IUPAC system distinguishes between them when we come to the chapters on those particular functional groups.)

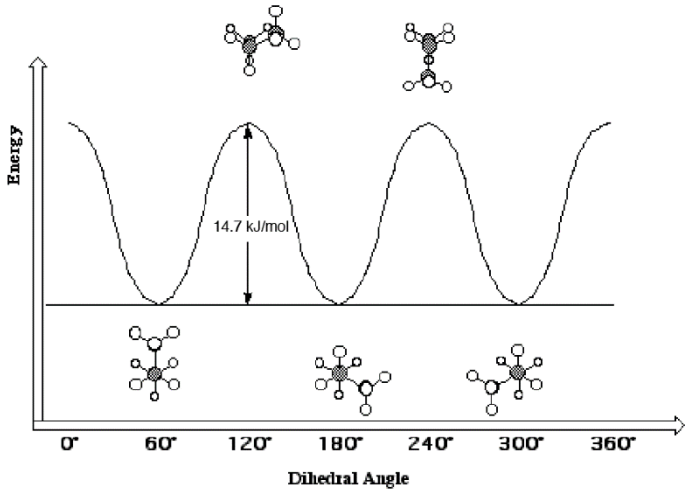
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Conformations of Alkanes and Cycloalkanes

Problem 2.32

Torsional strain resulting from eclipsed C—H bonds is approximately 4.2 kJ (1.0 kcal)/mol, and that for eclipsed C—H and C—CH_3 bonds is approximately 6.3 kJ (1.5 kcal)/mol. Given this information, sketch a graph of energy versus dihedral angle for propane.



Notice that the energy of the eclipsed conformations is 14.7 kJ/mol higher in energy than the staggered conformations. This is because each eclipsed conformation has two C—H bonds eclipsed with other C—H bonds (worth 4.2 kJ/mol each) and one C—H bond eclipsed to a C—CH_3 bond (worth 6.3 kJ/mol).

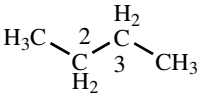
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Problem 2.33

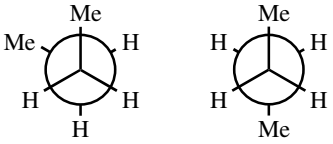
How many different staggered conformations are there looking down the C2–C3 bond of butane? How many different eclipsed conformations are there?

Looking down the C2–C3 bond, there are two staggered conformations and two eclipsed conformations for butane.

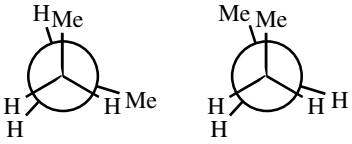


Butane

Staggered



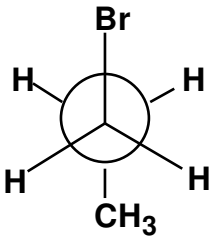
Eclipsed



Problem 2.34

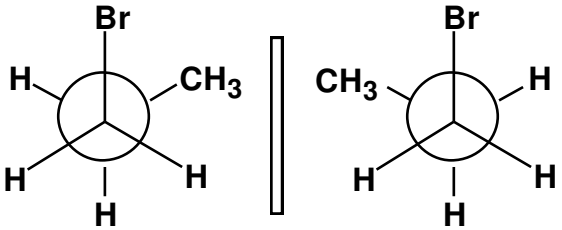
Consider 1-bromopropane, $CH_3CH_2CH_2Br$.

(a) Draw a Newman projection for the conformation in which —CH_3 and —Br are anti (dihedral angle 180°).



lowest in energy

(b) Draw Newman projections for the conformations in which —CH_3 and —Br are gauche (dihedral angles 60° and 300°).



related by reflection

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(c) Which of these is the lowest energy conformation?

The anti (dihedral angle 180°) is the lowest energy conformation.

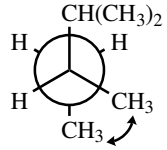
(d) Which of these conformations, if any, are related by reflection?

The two gauche conformations are of equal energy and are related by reflection.

Problem 2.35

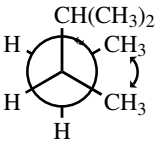
Consider 2,3-dimethylpentane along bond C(3)-C(4) and draw the following:

(a) The lowest energy staggered conformation(s)



Lowest energy
Methyl groups gauche

(b) The highest energy staggered conformation(s)



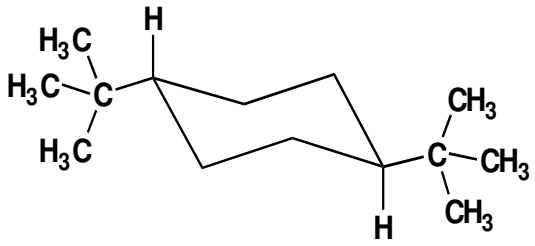
Highest energy
Gauche interaction between isopropyl and methyl groups
Gauche interaction between methyl groups

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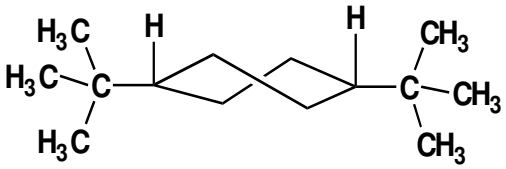
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Problem 2.36

trans-1,4-Di-*tert*-butylcyclohexane exists in a normal chair conformation. *cis*-1,4-Di-*tert*-butylcyclohexane, however, adopts a twist-boat conformation. Draw both isomers and explain why the *cis* isomer is more stable in a twist-boat conformation.



The *trans* isomer in the chair form



The *cis* isomer in the twist-boat form

The *cis* isomer adopts a twist-boat conformation because each of the bulky *tert*-butyl groups can be in a pseudo-equatorial position. If the *cis* isomer existed in a normal chair conformation, then one *tert*-butyl group would be equatorial, while the other would be forced axial resulting in a large nonbonded interaction strain.

Problem 2.37

From studies of the dipole moment of 1,2-dichloroethane in the gas phase at room temperature (25°C), it is estimated that the ratio of molecules in the anti conformation to gauche conformation is 7.6 to 1. Calculate the difference in Gibbs free energy between these two conformations.

$$\Delta G° = -RT \ln K_{eq}$$

$$K_{eq} = \frac{7.6}{1} = 7.6 \quad \text{so } \ln K_{eq} = 2.0$$

Plugging in the gas constant ($R = 8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and temperature ($T = 298\ \text{K}$)

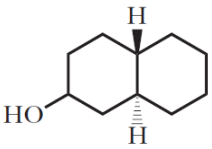
$$\Delta G° = -(8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})(2.0) = 5.0 \times 10^{3}\ \text{J/mol} = \boxed{5.0\ \text{J/mol}}$$

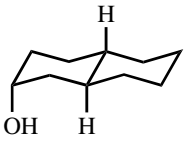
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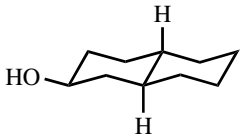
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Problem 2.38

The orientation of the hydroxyl group in the structure below is not specified, so two stereoisomers are possible. Draw structural formulas for both. Show each ring in its most stable conformation. Which of these isomers is more stable?



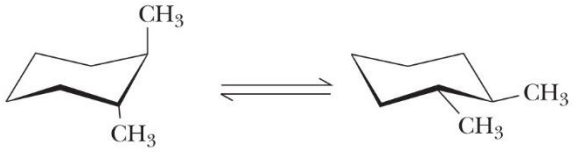




The two isomers shown differ in the orientation of the hydroxyl group attached to the ring. In the isomer on the left, the hydroxyl group is held in the axial position and has diaxial interactions with other hydrogens on the ring. In the isomer on the right, the hydroxyl group is in the equatorial position and does not have any diaxial interactions. Therefore, the isomer on the right is more stable.

Problem 2.39

Following are the alternative chair conformations for *trans*-1,2-dimethylcyclohexane.



***trans*-1,2-Dimethylcyclohexane**

(a) Estimate the difference in free energy between these two conformations.

As described in Example 2.11, the difference in energy between a diaxial and diequatorial dimethyl cyclohexane conformation is 14.56 kJ (3.5 kcal)/mol. In the case of *trans*-1,2-dimethylcyclohexane, in the diequatorial conformation, there is also a gauche interaction between the two methyl groups that must be considered. Estimate the gauche interaction to be 3.8 kJ (0.91 kcal)/mol based on the gauche interaction in butane (Figure 2.9). This gauche interaction introduces a small amount of steric strain into the more stable diequatorial conformation reducing the absolute value of the total $\Delta G°$ as follows:

$$\Delta G° = -14.56 \text{ kJ } (3.5\text{kcal})/\text{mol} + 3.8\text{kJ } (0.91 \text{ kcal})/\text{mol} = \boxed{-10.76 \text{ kJ } (2.59 \text{ kcal})/\text{mol}}$$

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(b) Given your value in (a), calculate the percent of each chair present in an equilibrium mixture of the two at 25°C.

$\Delta G° = -RT \ln K_{eq}$

Plugging in the gas constant ($R = 8.314$ J•K^{-1}•mol^{-1}) temperature ($T = 298$ K) and value of $\Delta G°$ for the equilibrium (-10.76 kJ (2.59 kcal)/mol) gives the following

$$\ln K_{eq} = \frac{-(-10,760 \text{ J/mol})}{8.314 \text{ J•K}^{-1}\text{•mol}^{-1} \times 298 \text{ K}} = 4.343$$

$$K_{eq} = \frac{76.9}{1} = \frac{\text{diequatorial}}{\text{diaxial}}$$

Based on this calculation, at equilibrium, there is 1.3% in the diaxial chair conformation, and 98.7% in the diequatorial chair conformation.

Problem 2.40 Think–Pair–Share

Neopentane is the common name for 2,2-dimethylpropane.

(a) Draw the bond line representation of this molecule.

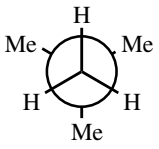


Neopentane

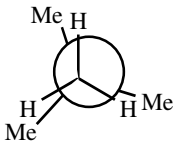
(b) Draw the different Newman projections for each conformation of neopentane.

Only two different types of Newman projections exist as shown next.

Staggered



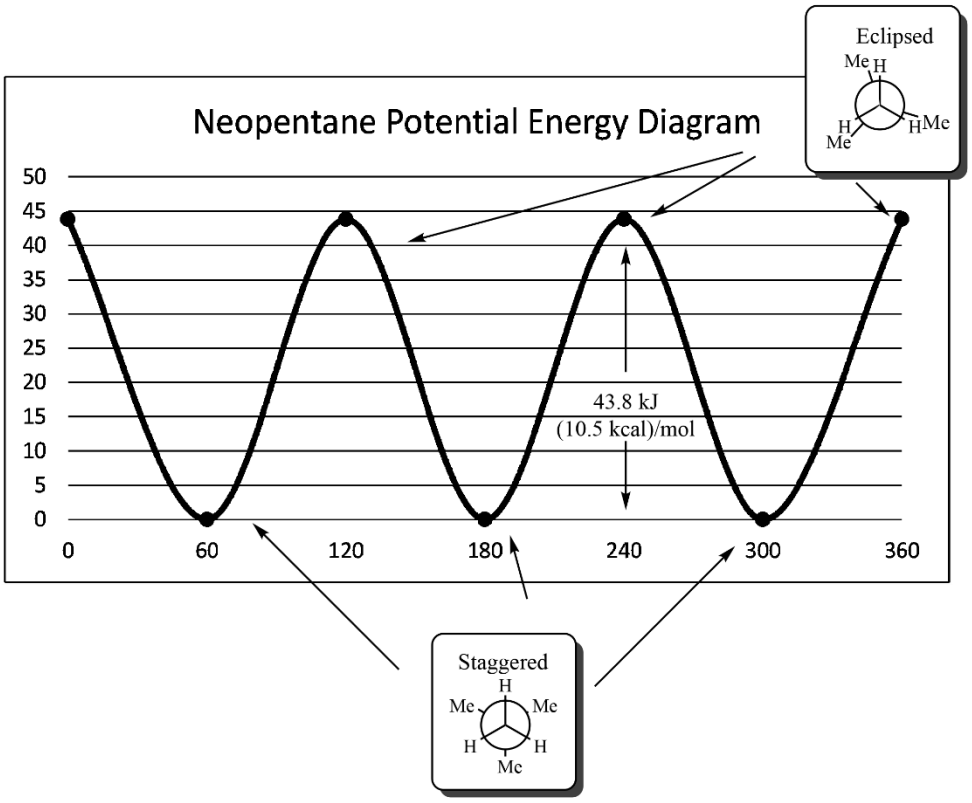
Eclipsed



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(c) Sketch the potential energy relationship corresponding to a full 360° rotation around the C(1)-C(2) bond.



(d) Estimate the energy difference between local maxima and minima that correspond to high or low energy conformations of neopentane. Clearly indicate the relative energies of stable conformations (energy minima) and transition points (energy maxima) on the graph in part (c).

The staggered conformation has no relative energy cost. The eclipsed conformation has three Me/H eclipsing interactions with a cost of 14.6 kJ (3.5 kcal)/mol each for a total of 43.8 kJ (10.5 kcal)/mol.

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Cis,Trans Isomerism in Cycloalkanes

Problem 2.41

What structural feature of cycloalkanes makes *cis,trans* isomerism in them possible?

Because the atoms are connected in a ring, the C—C bonds cannot rotate around all 360°. As a result, groups on the ring have a fixed relationship with respect to each other, either *cis* or *trans*.

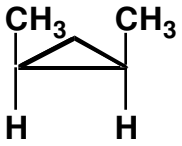
Problem 2.42

Is *cis,trans* isomerism possible in alkanes?

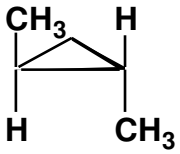
The C—C bonds in alkanes can rotate 360°, so *cis,trans* isomerism is not possible.

Problem 2.43

Draw line-angle formulas for the *cis* and *trans* isomers of 1,2-dimethylcyclopropane.



***cis*-1,2-Dimethylcyclopropane**



***trans*-1,2-Dimethylcyclopropane**

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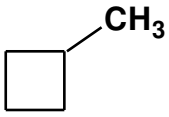
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Problem 2.44

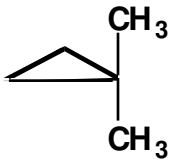
Name and draw structural formulas for all cycloalkanes with molecular formula C_5H_{10}. Include *cis* and *trans* isomers as well as constitutional isomers.



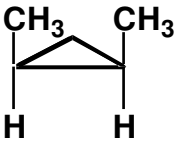
Cyclopentane



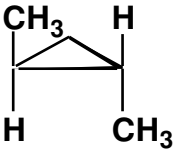
Methylcyclo-
butane



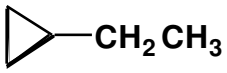
1,1-Dimethyl-
cyclopropane



cis-1,2-Dimethyl-
cyclopropane



trans-1,2-Dimethyl-
cyclopropane

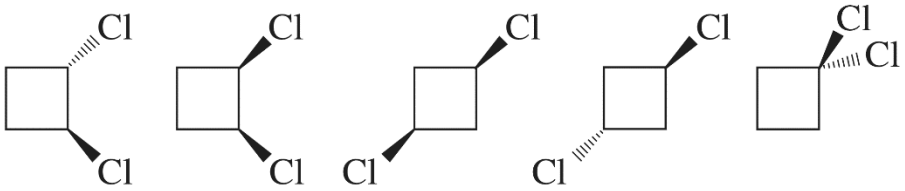


Ethylcyclopropane

Problem 2.45

How many different isomers are possible for dichlorocyclobutane? Draw a line angle formula for each isomer.

Five different isomers exist:



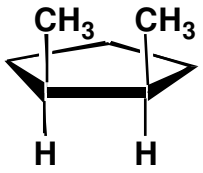
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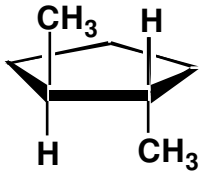
Problem 2.46

Using a planar pentagon representation for the cyclopentane ring, draw structural formulas for the *cis* and *trans* isomers of the following.

(a) 1,2-Dimethylcyclopentane

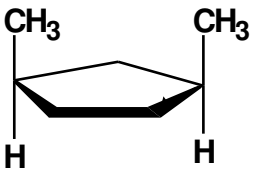


***cis*-1,2-Dimethylcyclopentane**

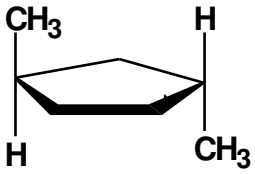


***trans*-1,2-Dimethylcyclopentane**

(b) 1,3-Dimethylcyclopentane



***cis*-1,3-Dimethylcyclopentane**

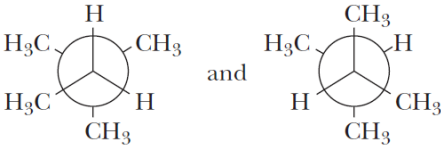


***trans*-1,3-Dimethylcyclopentane**

Problem 2.47

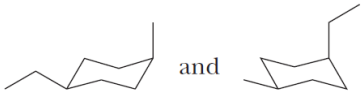
Determine whether the following pairs of structures represent constitutional isomers, conformational isomers, or stereoisomers.

(a)



Constitutional isomers

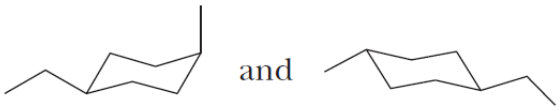
(b)



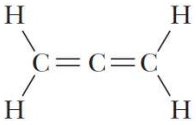
Conformational isomers

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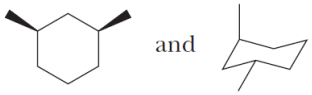
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(c)  and

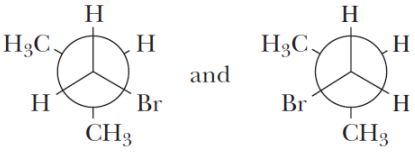
Stereoisomers

(d)  and $H_3C—C{\equiv}C—H$

Constitutional isomers

(e) 

Stereoisomers

(f) 

Conformational isomers

Problem 2.48

Gibbs free energy differences between axial-substituted and equatorial-substituted chair conformations of cyclohexane were given in Table 2.4.

(a) Calculate the ratio of equatorial to axial *tert*-butylcyclohexane at 25°C.

According to the value given in Table 2.4, the equatorial *tert*-butylcyclohexane is 21 kJ/mol more stable than the axial conformation.

Rearranging $\Delta G° = -RT \ln K_{eq}$ gives $\ln K_{eq} = \dfrac{-\Delta G°}{RT}$

Plugging in the gas constant (R = 8.314 J•K^{-1}•mol^{-1}) and temperature (T = 298 K) as well as the value for $\Delta G°$ converted to J/mol gives

$$\ln K_{eq} = \frac{21{,}000 \text{ J/mol}}{(8.314 \text{ J•K}^{-1}\text{•mol}^{-1})(298 \text{ K})} = 8.5$$

$$K_{eq} = e^{8.5} = 4.9 \times 10^3$$

So the ratio of equatorial to axial is 4.9×10^3:1

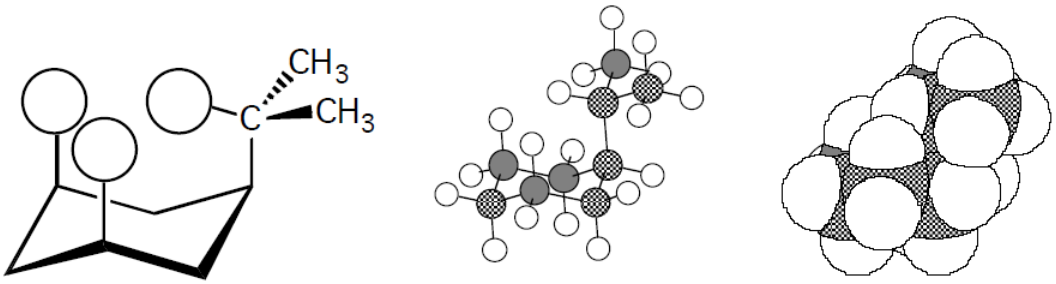
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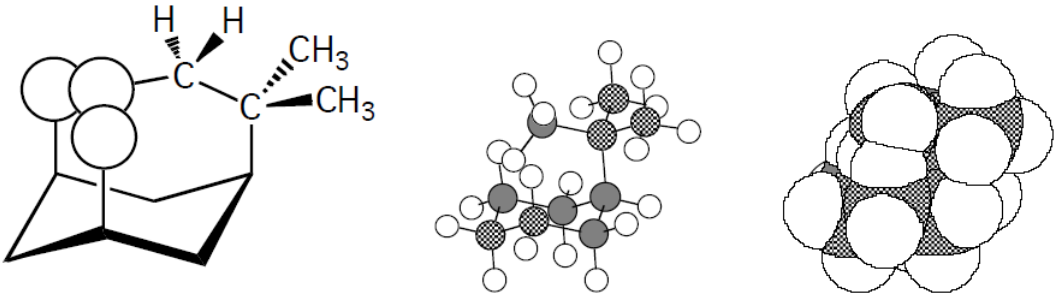
(b) Explain why the conformational equilibria for methyl, ethyl, and isopropyl substituents are comparable but the conformational equilibrium for *tert*-butylcyclohexane lies considerably farther toward the equatorial conformation.

Rotation is possible about the single bond connecting the axial substituent to the ring. Axial methyl, ethyl, and isopropyl groups can assume a conformation where a hydrogen creates the 1,3-diaxial interactions. With a *tert*-butyl substituent, however, a bulkier —CH_3 group must create the 1,3-diaxial interaction. Because of the increased steric strain (nonbonded interactions) created by the axial *tert*-butyl, the energy of the axial conformation is considerably greater than that of the equatorial conformation.

As seen next, an axial isopropyl group can adopt a conformation with only a minimal 1,3 diaxial interaction:



On the other hand, an axial *tert*-butyl group leads to a very severe 1,3 diaxial interaction:



Problem 2.49

When cyclohexane is substituted by an ethynyl group, —C≡CH, the energy difference between axial and equatorial conformations is only 1.7 kJ (0.41 kcal)/mol. Compare the conformational equilibrium for methylcyclohexane with that for ethynylcyclohexane and account for the difference between the two.

For the ethynyl case, using the same equation as in part (a) of 2.37 gives:

$$\ln K_{eq} = \frac{1,700\ \text{J/mol}}{(8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})} = 0.69$$

$$K_{eq} = e^{0.69} = 2.0$$

So the ratio of equatorial to axial ethynyl is 2:1

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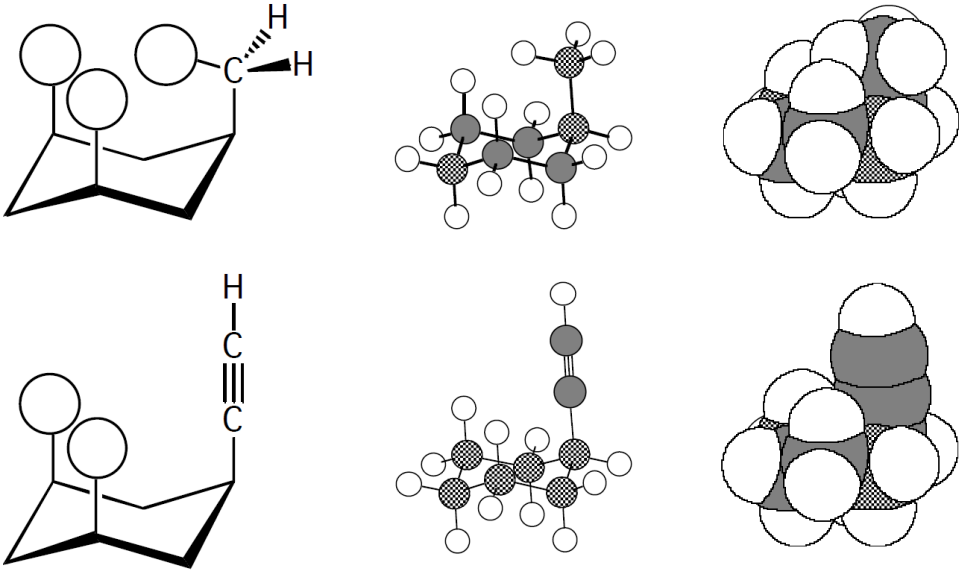
Using the value of 7.28 kJ/mol given in Table 2.4 for the methyl case gives:

$$\ln K_{eq} = \frac{7{,}280 \text{ J/mol}}{(8.314 \text{ J•K}^{-1}\text{•mol}^{-1})(298 \text{ K})} = 2.94$$

$$K_{eq} = e^{2.94} = 18.9$$

So the ratio of equatorial to axial methyl is 18:9:1

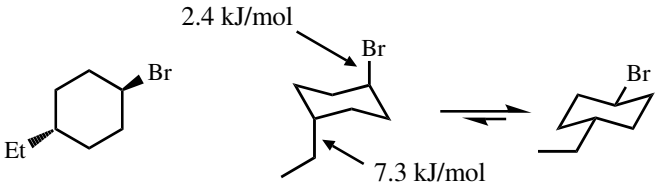
The ratios make sense because as can be seen with the following structures and models, the bulkier methyl group is expected to have more severe 1,3 diaxial interactions than the linear —C≡CH group.



Problem 2.50

Calculate the difference in Gibbs free energy in kilojoules per mole between the alternative chair conformations of:

(a) *trans*-1-Bromo-4-ethylcyclohexane

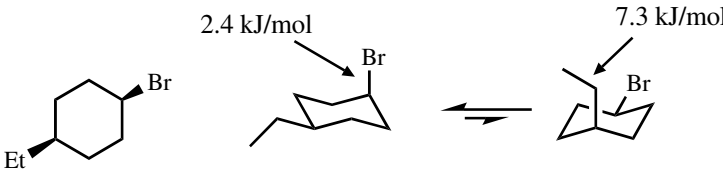


The chair on the right is favored because both the bromo and ethyl groups are equatorial. Using the data from Table 2.4, the chair on the left is less stable by 7.3 kJ/mol (ethyl group axial) + 2.4 kJ/mol (Br axial) = 9.7 kJ/mol.

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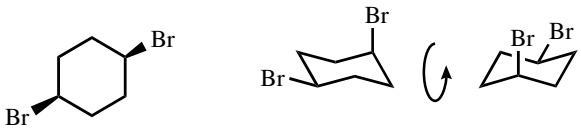
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(b) *cis*-1-Bromo-4-ethylcyclohexane



The chair on the left is favored because an axial —Br group is more favorable than an axial —CH_2CH_3 group. Using the data from Table 2.4, the chair on the left has an axial —Br group that costs 2.4 kJ/mol, while the chair on the right has an axial —CH_2CH_3 that costs 7.3 kJ/mol. The chair on the left is thus more stable by 7.3 kJ/mol – 2.4 kJ/mol = 4.9 kJ/mol.

(c) *cis*-1,4-Dibromocyclohexane



The two chair conformations are equivalent so there is no difference in Gibbs free energy between them. One —Br group is axial and the other is equatorial.

Problem 2.51

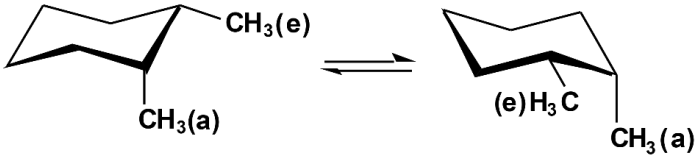
Draw the alternative chair conformations for the *cis* and *trans* isomers of 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, and 1,4-dimethylcyclohexane.

(a) Indicate by a label whether each methyl group is axial or equatorial.

(b) For which isomer(s) are the alternative chair conformations of equal stability?

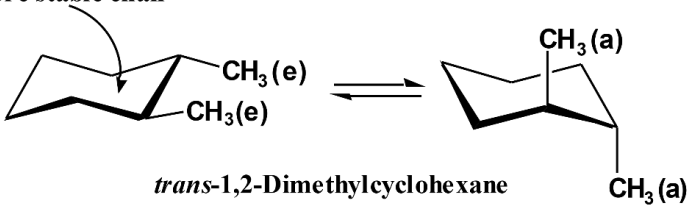
(c) For which isomer(s) is one chair conformation more stable than the other?

Cis and *trans* isomers are drawn as pairs. The more stable chair is labeled in cases where there is a difference.



***cis*-1,2-Dimethylcyclohexane**
(chairs of equal stability)

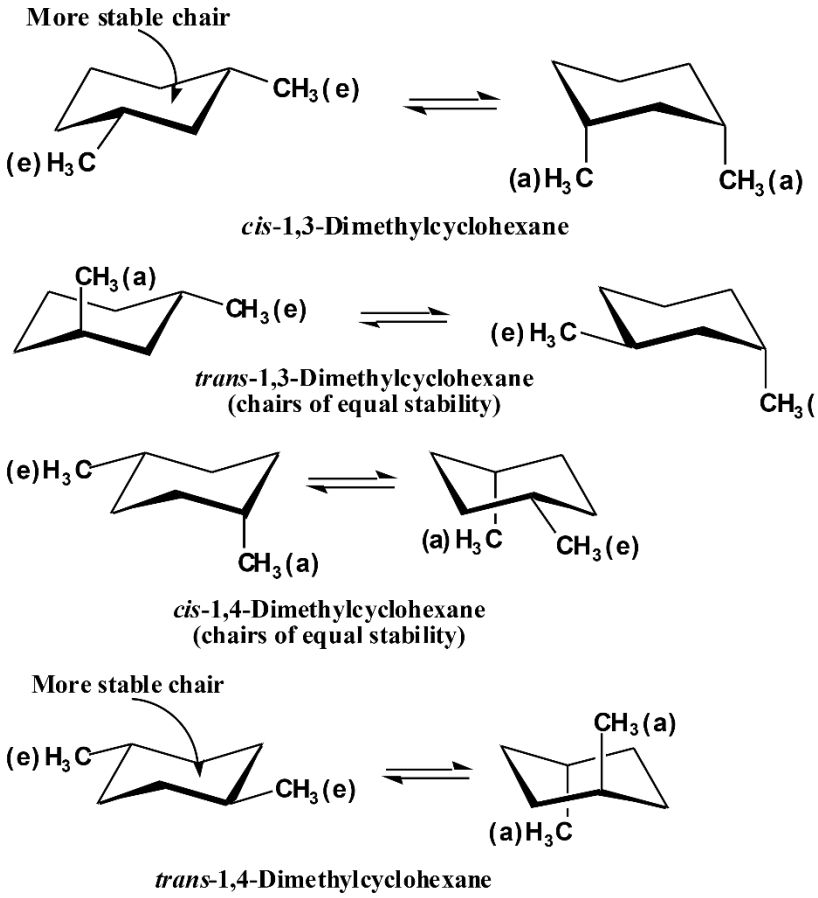
More stable chair



***trans*-1,2-Dimethylcyclohexane**

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Problem 2.52

Use your answers from Problem 2.51 to complete the table showing correlations between *cis,trans* and axial,equatorial for disubstituted derivatives of cyclohexane.

Position of Substitution	*cis*	*trans*
1,4-	a,e or e,a	e,e or a,a
1,3-	___ or ___	___ or ___
1,2-	___ or ___	___ or ___

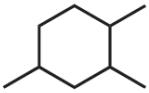
These relationships are summarized in the following table.

Position of Substitution	*cis*	*trans*
1,4	a,e or e,a	e,e or a,a
1,3	e,e or a,a	a,e or e,a
1,2	a,e or e,a	e,e or a,a

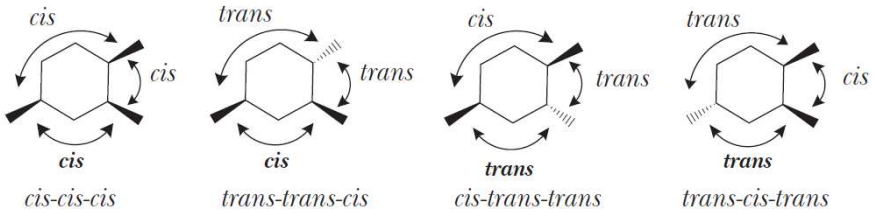
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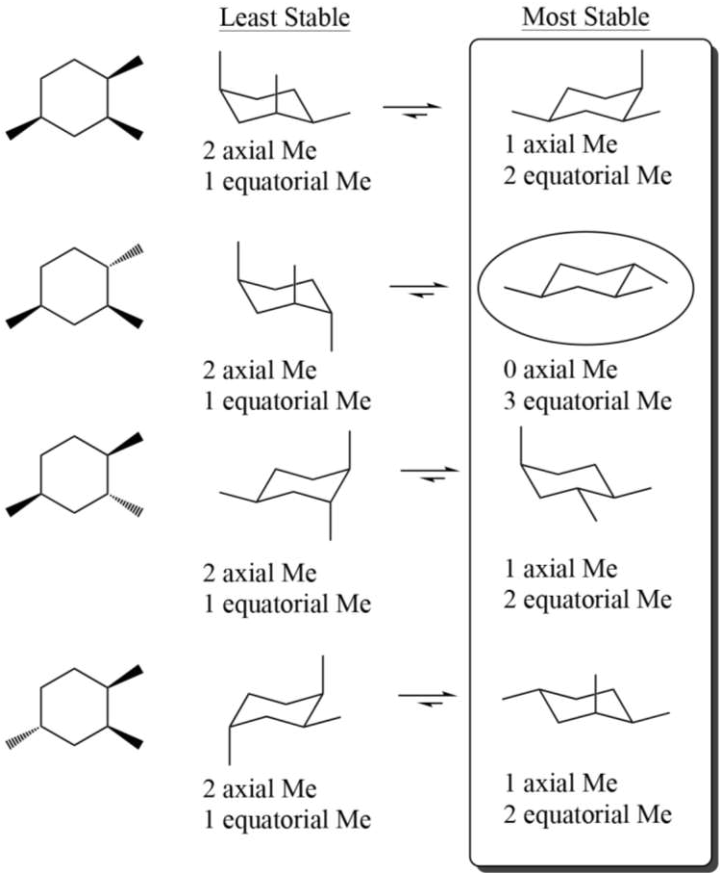
Problem 2.53 Think–Pair–Share



Four different *cis-trans* combinations exist for the structure shown above:



(a) Draw the two possible chair conformations for each structure and determine which chair conformation is most stable. Why is a given chair conformation more stable than the other?



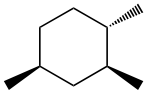
The chair conformations on the right are most stable because they contain the greatest number of low-energy equatorial substituents.

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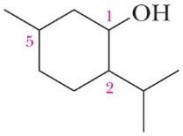
(b) Comparing the most stable chair conformations of each, which of the four isomers above would be the most stable?

Of the chair conformations shown, the highlighted chair that has three equatorial substituents and no axial substituents is most stable.



Problem 2.54

There are four *cis,trans* isomers of 2-isopropyl-5-methylcyclohexanol:



2-Isopropyl-5-methylcyclohexanol

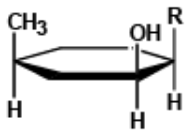
(a) Using a planar hexagon representation for the cyclohexane ring, draw structural formulas for the four *cis,trans* isomers.

(b) Draw the more stable chair conformation for each of your answers in part (a).

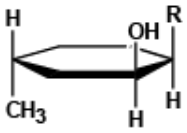
(c) Of the four *cis,trans* isomers, which is most stable? (*Hint:* If you answered this part correctly, you picked the isomer found in nature and given the name menthol.)

Following are planar hexagon representations for the four *cis, trans* isomers. In each, the isopropyl group is shown by the symbol R-. One way to arrive at these structural formulas is to take one group as a reference and then arrange the other two groups in relation to it. In these drawings, —OH is taken as the reference and placed above the plane of the ring. Once —OH is fixed, there are only two possible arrangements for the isopropyl group on carbon 2; either *cis* or *trans* to —OH. Similarly, there are only two possible arrangements for the methyl group on carbon-5; either *cis* or *trans* to —OH. Note that even if you take another substituent as a reference, and even if you put the reference below the plane of the ring, there are still only four *cis,trans* isomers for this compound.

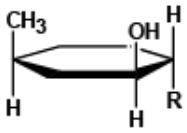
(a)



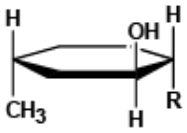
***cis*-2-Isopropyl-*cis*-5-methyl-cyclohexanol**



***cis*-2-Isopropyl-*trans*-5-methyl-cyclohexanol**



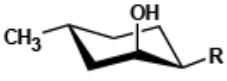
***trans*-2-Isopropyl-*cis*-5-methyl-cyclohexanol**



***trans*-2-Isopropyl-*trans*-5-methyl-cyclohexanol**

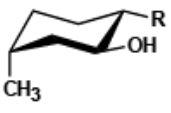
(b),(c)







Most stable chair (all equatorial)



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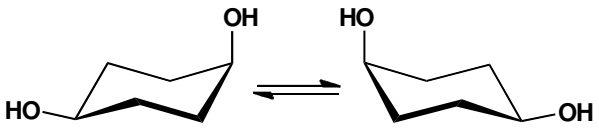
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Problem 2.55

Draw alternative chair conformations for each substituted cyclohexane and state which chair is more stable.

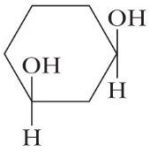
(a)

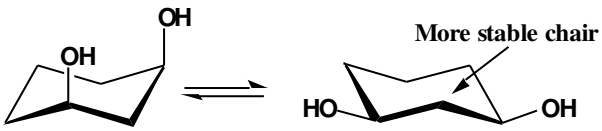




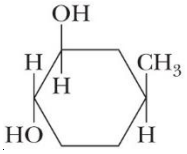
(Chairs of equal stability)

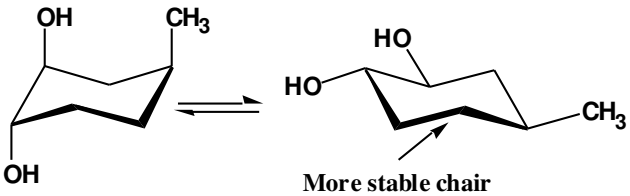
(b)





(c)

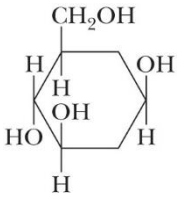


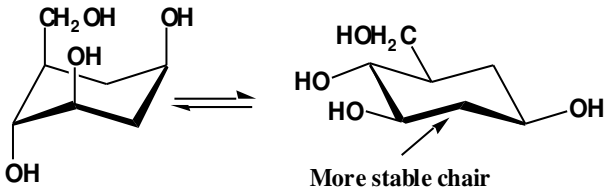


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(d)

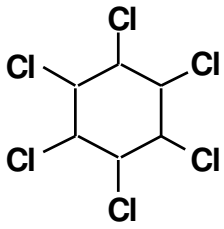




Problem 2.56

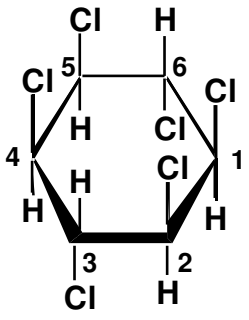
1,2,3,4,5,6-Hexachlorocyclohexane shows *cis,trans* isomerism. At one time, a crude mixture of these isomers was sold as an insecticide. The insecticidal properties of the mixture arise from one isomer, known as lindane, which is *cis*-1,2,4,5-*trans*-3,6-hexachlorocyclohexane.

(a) Draw a structural formula for 1,2,3,4,5,6-hexachlorocyclohexane disregarding, for the moment, the existence of *cis,trans* isomerism. What is the molecular formula of this compound?



$C_6H_6Cl_6$

(b) Using a planar hexagon representation for the cyclohexane ring, draw a structural formula for lindane.



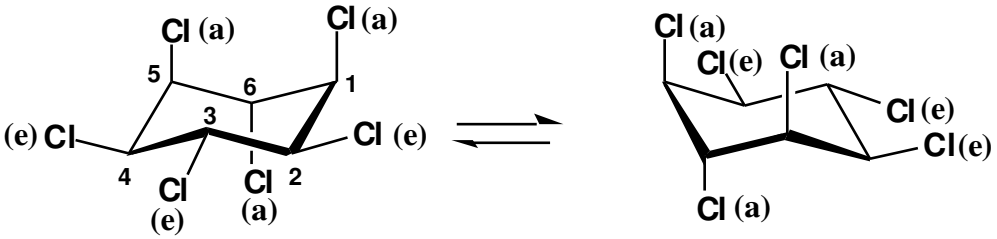
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(c) Draw a chair conformation for lindane and label which chlorine atoms are axial and which are equatorial.

(d) Draw the alternative chair conformation of lindane and again label which chlorine atoms are axial and which are equatorial.

(e) Which of the alternative chair conformations of lindane is more stable? Explain.



The two chairs are of equal stability; in each three —Cl atoms are axial and three are equatorial

Physical Properties

Problem 2.57

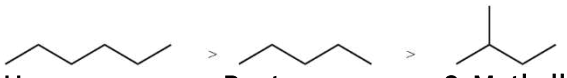
In Problem 2.24, you drew structural formulas for all isomeric alkanes with molecular formula C_7H_{16}. Predict which isomer has the lowest boiling point and which has the highest boiling point.

Names and boiling points of these isomers are given in the solution to Problem 2.24. The isomer with the lowest boiling point is 2,2-dimethylpentane, bp 79.2°C. The isomer with the highest boiling point is heptane, bp 94.8°C.

Problem 2.58

Rank the following compounds from highest to lowest boiling point.

Pentane Hexane 2-Methylbutane



Hexane > **Pentane** > **2-Methylbutane**

C_6H_{14} C_5H_{12} C_5H_{12}

Hexane has the highest boiling point because it has the longest molecular chain and therefore has the greatest number of dispersion forces associated with it. Pentane and 2-methylbutane are constitutional isomers; however, pentane has a greater boiling point because it is linear, not branched, and therefore has a greater number of dispersion forces.

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Problem 2.59

What generalization can you make about the densities of alkanes relative to the density of water?

All alkanes that are liquid at room temperature are less dense than water (The O atom of H_2O has a larger atomic mass than the C atom of alkanes). This is why alkanes such as those in gasoline and petroleum float on water.

Problem 2.60

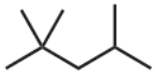
What unbranched alkane has about the same boiling point as water? (Refer to Table 2.5 on the physical properties of alkanes.) Calculate the molecular weight of this alkane and compare it with that of water.

Heptane, C_7H_{16}, has a boiling point of 98.4°C and a molecular weight of 100. Its molecular weight is approximately 5.5 times that of water. Although considerably smaller, the water molecules are held together by hydrogen bonding while the much larger heptane molecules are held together only by relatively weak dispersion forces.

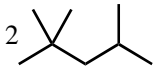
Reactions of Alkanes

Problem 2.61

Complete and balance the following combustion reactions. Assume that each hydrocarbon is converted completely to carbon dioxide and water.

(a)  + $O_2 \rightarrow$

Iso-octane
(gasoline component)

2  **+ 25 O_2 → 16 CO_2 + 18 H_2O**

(b) Heptane + $O_2 \rightarrow$

Heptane + 11 $O_2 \rightarrow$ 7 CO_2 + 8 H_2O

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(c) Butane+ $O_2 \rightarrow$

2 Butane + 13 $O_2 \rightarrow$ 8 CO_2 + 10 H_2O

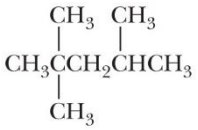
(d) $CH_3(CH_2)_{19}CH_3 + O_2 \rightarrow$

Paraffin wax component

$CH_3(CH_2)_{19}CH_3$ + 32 $O_2 \rightarrow$ 21 CO_2 + 22 H_2O

*Problem 2.62

Following are heats of combustion per mole for methane, propane, and 2,2,4-trimethyl pentane. Each is a major source of energy. On a gram-for-gram basis, which of these hydrocarbons is the best source of heat energy?

Hydrocarbon	Component of	ΔH^0 [kJ (kcal)/mol]
CH_4	Natural gas	−891 (−213)
$CH_3CH_2CH_3$	LPG	−2220 (−531)
	Gasoline	−5452 (−1304)

On a gram-per-gram basis, methane is the best source of heat energy.

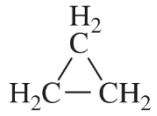
Hydrocarbon	Molecular Weight	Heat of Combustion (kJ/mol)	Heat of Combustion (kJ/gram)
Methane	**16.04**	**−891**	**−55.5**
Propane	**44.09**	**−2220**	**−50.4**
2,2,4-Trimethylpentane	**114.2**	**−5452**	**−47.7**

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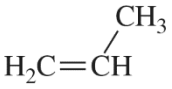
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Problem 2.63

The following are structural formulas and heats of combustion of cyclopropane and propene. Which of these compounds is more stable? Explain.



Cyclopropane
–2091.kJ (–500 kcal)/mol



Propene
–2058 kJ (–492 kcal)/mol

These molecules are constitutional isomers, so their heats of combustion are directly comparable. The molecule with the smaller (less negative) heat of combustion is the more stable, having less energy to release during the combustion process. As a result, propene is the more stable compound.

Problem 2.64

Without consulting tables, arrange these compounds in order of decreasing (less negative) heat of combustion: hexane, 2-methylpentane, and 2,2-dimethylbutane.

Branching increases stability of an alkane. Therefore, the more highly branched the isomer, the smaller (less negative) the heat of combustion. The molecules listed in order of decreasing heat of combustion turn out to be exactly as they were listed in the question: Hexane, 2-Methylpentane, 2,2-Dimethylbutane.

Problem 2.65

Which would you predict to have the larger (more negative) heat of combustion, *cis*-1,4-dimethylcyclohexane or *trans*-1,4-dimethylcyclohexane?

The less stable molecule will have the larger (more negative) heat of combustion. Because these molecules are constitutional isomers with virtually identical ring strain, any difference in energy between them must be the result of differences in conformational stability. As listed in the answer to Problem 2.39, the *cis* isomer has two chair conformations of equal energy, each one with one axial and one equatorial methyl group. The *trans* isomer has chair conformations of different stability, the more stable of which is the diequatorial conformation that has no diaxial interactions. By virtue of having diaxial interactions in both chair conformations, the *cis* isomer is higher in energy and thus will have the larger (more negative) heat of combustion.

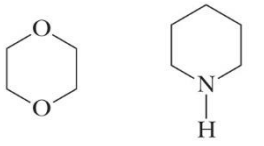
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LOOKING AHEAD

Problem 2.66

Following are structural formulas for 1,4-dioxane and piperidine. 1,4-Dioxane is a widely used solvent for organic compounds. Piperidine is found in small amounts in black pepper (*Piper nigrum*).



1,4-Dioxane **Piperidine**

(a) Complete the Lewis structure of each compound by showing all unshared electron pairs.



1,4-Dioxane **Piperidine**

(b) Predict bond angles about each carbon, oxygen, and nitrogen atom.

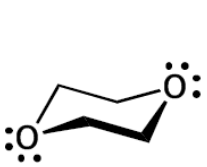
Each carbon, oxygen, and nitrogen atom is sp^3 hybridized, so predict bond angles near 109.5° for all of them.

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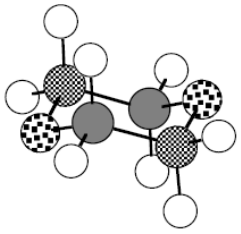
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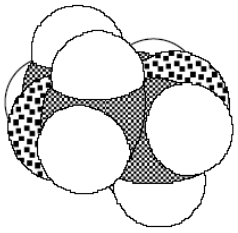
(c) Describe the most stable conformation of each ring and compare these conformations with the chair conformation of cyclohexane.

Both molecules have conformations analogous to chair cyclohexane, because in both cases this conformation minimizes torsional and angle strain.



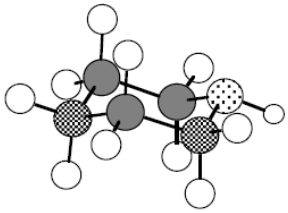
1,4-Dioxane

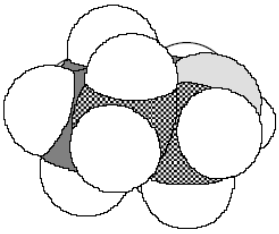






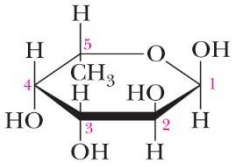
Piperidine





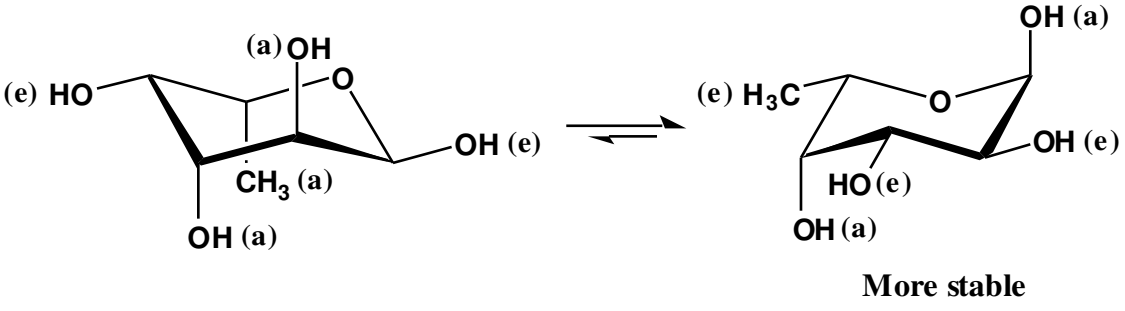
Problem 2.67

Following is a planar hexagon representation of L-fucose, a sugar component of the determinants of the A, B, O blood group typing. For more on this system of blood typing, see "Chemical Connections: A, B, AB, and O Blood Group Substances" in Chapter 25.



L-Fucose

(a) Draw the alternative chair conformations of L-fucose.



More stable

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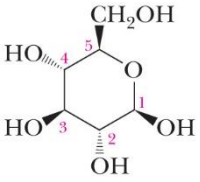
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(b) Which of them is more stable? Explain.

The structure on the right is more stable because it has only two axial —OH groups and three equatorial groups, the —CH_3 group and two —OH groups. The structure on the left has three axial groups so it will have the greater nonbonded interaction strain.

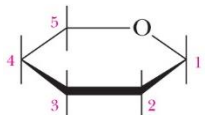
Problem 2.68

On the left is a stereorepresentation of glucose (we discuss the structure and chemistry of glucose in Chapter 25).

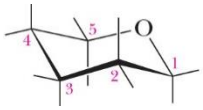


Glucose

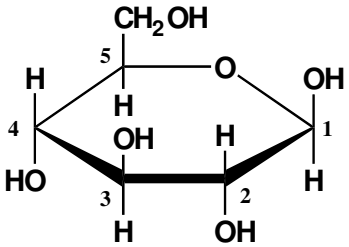
(a)



(b)



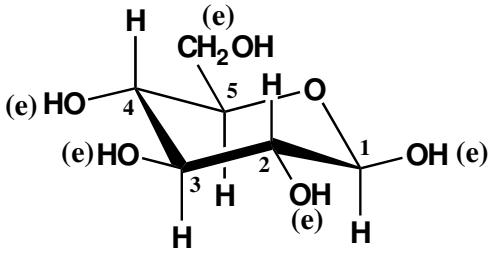
(a) Convert the stereorepresentation on the left to a planar hexagon representation.



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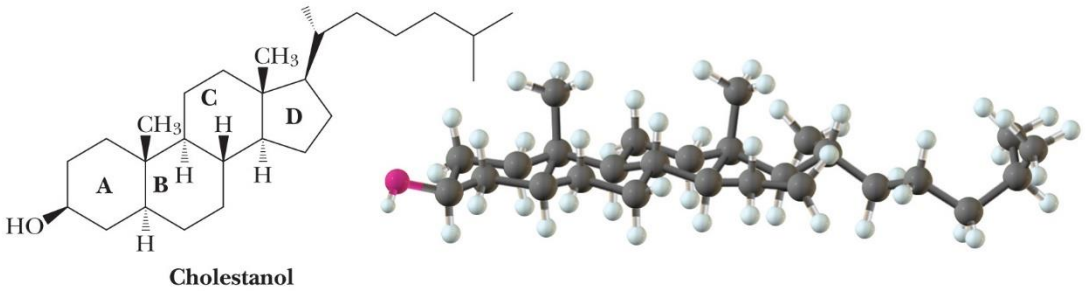
(b) Convert the stereorepresentation on the left to a chair conformation. Which substituent groups in the chair conformation are equatorial? Which are axial?



All of the substituents are equatorial, making this a particularly stable chair conformation.

Problem 2.69

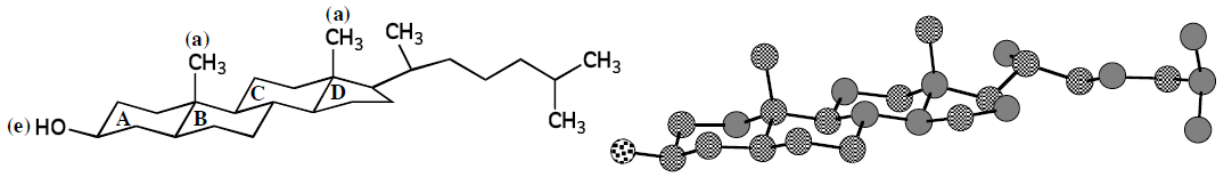
Following is the structural formula and a ball-and-stick model of cholestanol. The only difference between this compound and cholesterol is that cholesterol has a carbon-carbon double bond in ring B.



Cholestanol

(a) Describe the conformation of rings A, B, C, and D in cholestanol.

As can be seen in the following structures, the conformations of the six-membered rings, that is, A, B, and C, are all chairs. The conformation of the five-membered ring, ring D, is puckered (envelope). These conformations all represent preferred conformations and the ring fusions between rings prevent chair-to-chair interconversion. The result is that the A, B, C, D ring systems of steroids such as cholestanol are relatively rigid molecular frameworks.



Ball-and-stick model of cholestanol with the H atoms removed for clarity.

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(b) Is the hydroxyl group on ring A axial or equatorial?

The hydroxyl group is equatorial.

(c) Consider the methyl group at the junction of rings A and B. Is it axial or equatorial to ring A? Is it axial or equatorial to ring B?

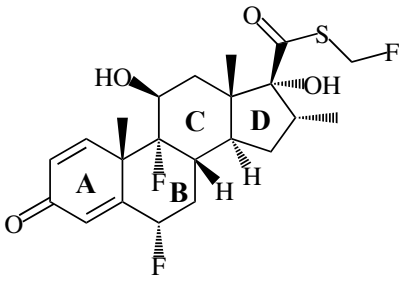
The methyl group at the A,B junction is axial to both rings A and B.

(d) Is the methyl group at the junction of rings C and D axial or equatorial to ring C?

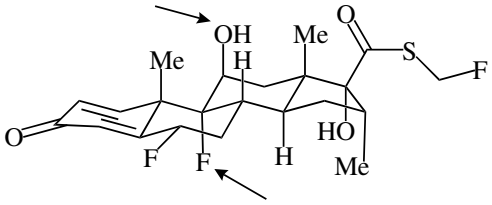
The methyl group at the C, D junction is axial to ring C.

Problem 2.70

Fluticasone is a pharmaceutical in the corticosteroid family of medicines. It acts as an anti-inflammatory that is used to treat nasal symptoms. The carbon backbone is similar to cholesterol and similarly contains *trans* ring junctions. Determine if the OH and F substituents attached to ring C are in equatorial or axial positions.



As seen from the depiction here, both the OH and F substituents on the C ring are in axial positions.

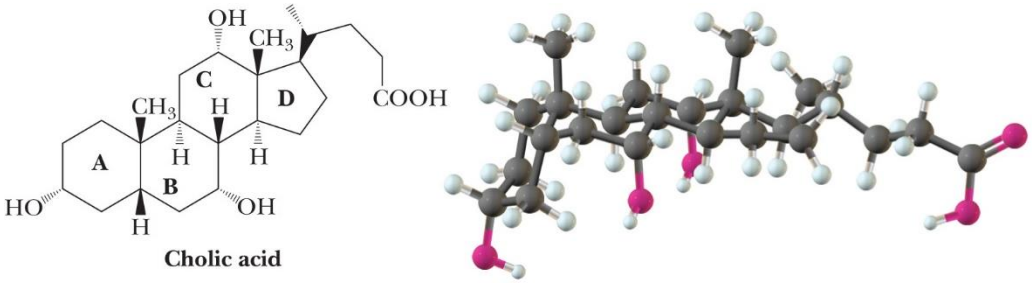


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*Problem 2.71

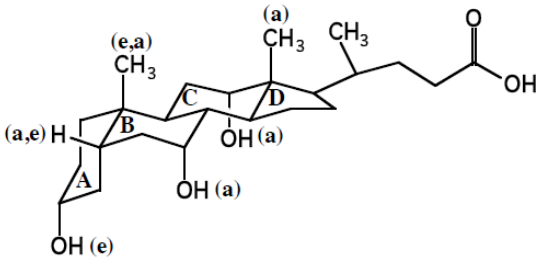
Following is the structural formula and a ball-and-stick model of cholic acid (Chapter 27), a component of human bile whose function is to aid in the absorption and digestion of dietary fats.

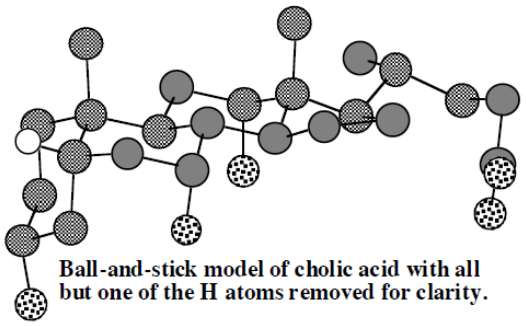


Cholic acid

(a) What is the conformation of ring A? of ring B? of ring C? of ring D?

As can be seen in the following structures, the conformations of all of the six-membered rings, that is, A, B, and C, are all chairs. The conformation of the five-membered ring, ring D, is puckered. These conformations all represent preferred conformations and the linkages between rings prevent chair-to-chair interconversion.





Ball-and-stick model of cholic acid with all but one of the H atoms removed for clarity.

(b) Are the hydroxyl groups on rings A, B, and C axial or equatorial to their respective rings?

The hydroxyl group on ring A is equatorial, the hydroxyl groups on rings B and C are axial.

(c) Is the methyl group at the junction of rings A and B axial or equatorial to ring A? Is it axial or equatorial to ring B?

The methyl group at the A, B ring junction is equatorial to ring A, but axial to ring B.

(d) Is the hydrogen at the junction of rings A and B axial or equatorial to ring A? Is it axial or equatorial to ring B?

The hydrogen atom at the junction of rings A and B is axial to ring A, but equatorial to ring B.

(e) Is the methyl group at the junction of rings C and D axial or equatorial to ring C?

The methyl group at the C, D junction is axial to ring C.

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