Chapter 3

Alkanes & Cycloalkane
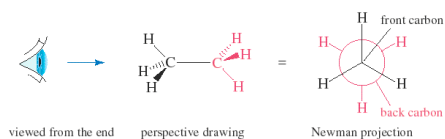
Conformations

Conformations of Alkanes: Rotation about Carbon–Carbon Bonds
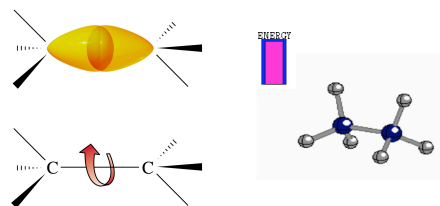
ENERGY

Conformational Analysis

### Drawing Acyclic Molecules

- Newman Projections

viewed from the end   perspective drawing   Newman projection

H front carbon
back carbon

Conformational Analysis

Drawing Acyclic Molecules

Newman projections: θ = 0°   θ = 60°   θ

Sawhorse structures:

eclipsed, θ = 0°   staggered, θ = 60°   skew, θ = anything else

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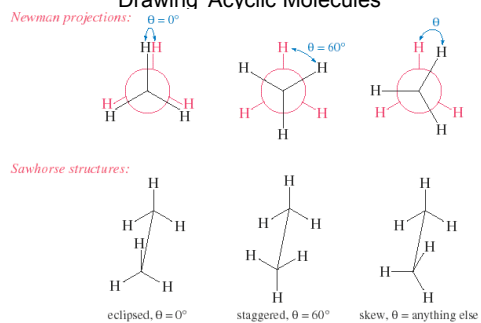
Question 3.1

- What is the IUPAC name for the compound represented by the Newman projection?
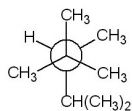
- A) 1-*tert*-Butyl-1-isopropylethane
- B) 1-*tert*-Butyl-3-methylbutane
- C) 2-isopropyl-3,3-dimethylbutane
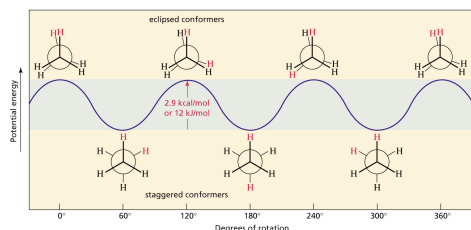- D) 2,2,3,4-tetramethylpentane

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Question 3.2

- What is the relationship between the Newman representations shown?

- A) identical
- B) constitutional isomers
- C) different conformations of the same compound
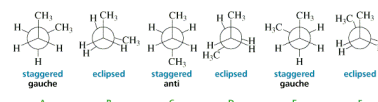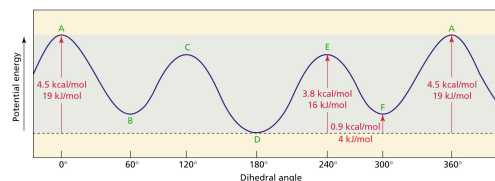- D) stereoisomers

Different Conformations of Ethane

- A staggered conformer is more stable than an eclipsed conformer
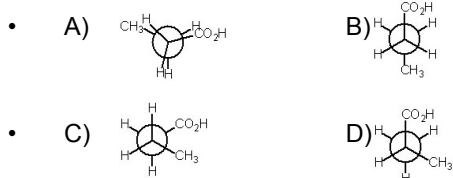- Torsional strain: repulsion between pairs of bonding electrons

Conformations of n-Butane

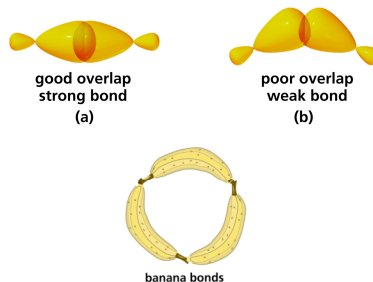- Steric strain: repulsion between the electron clouds of atoms or groups

Question 3.3

- Select the <u>most</u> stable conformation of butanoic acid.

- A)

- B)

- C)

- D)

Cycloalkanes: Ring Strain

- Angle strain results when bond angles deviate from the ideal 109.5° bond angle

good overlap
strong bond
(a)

poor overlap
weak bond
(b)

banana bonds

## The Shapes of Cycloalkanes: Planar or Nonplanar?

Adolf von Baeyer (19th century)

- Assumed cycloalkanes were planar polygons.
- Believed distortion of bond angles from 109.5° gives angle strain to some cycloalkanes.
- One for two is great in baseball.

Types of Strain

- *Torsional strain* strain that results from eclipsed bonds (measure of the dihedral angle)
- Van der Waals strain or (*Steric strain*) strain that results from atoms being too close together.
- *Angle strain* results from distortion of bond angles from normal values, for a tetrahedron 109.5°
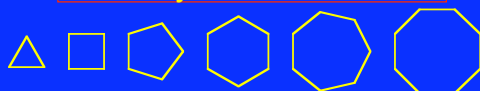
Measuring Strain in Cycloalkanes
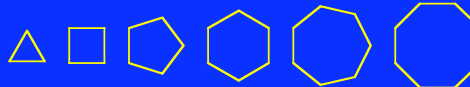
- Heats of combustion can be used to compare stabilities of isomers.
- But cyclopropane, cyclobutane, etc. are not isomers.
- All heats of combustion increase as the number of carbon atoms increase.

Measuring Strain in Cycloalkanes

- Therefore, divide heats of combustion by number of carbons and compare heats of combustion on a "per CH_2 group" basis.

Heats of Combustion in Cycloalkanes

Cycloalkane	kJ/mol	Per CH_2
Cyclopropane	2,091	697
Cyclobutane	2,721	681
Cyclopentane	3,291	658
Cyclohexane	3,920	653
Cycloheptane	4,599	657
Cyclooctane	5,267	658
Cyclononane	5,933	659
Cyclodecane	6,587	659

Heats of Combustion in Cycloalkanes

Cycloalkane	kJ/mol	Per CH_2

- According to Baeyer, cyclopentane should
- have less angle strain than cyclohexane.

Cyclopentane	3,291	658
Cyclohexane	3,920	653

- The heat of combustion per CH_2 group is
- less for cyclohexane than for cyclopentane.
- Therefore, cyclohexane has less strain than
- cyclopentane.

Question 3.4

- Which compound has the greatest torsional strain in the planar conformation?
- A) cyclopropane
- B) cyclobutane
- C) cyclopentane
- D) cyclohexane

Conformations of Cyclohexane

- Heat of combustion suggests that angle strain is unimportant in cyclohexane.

- Tetrahedral bond angles require nonplanar geometries.

- The chair and boat conformations.
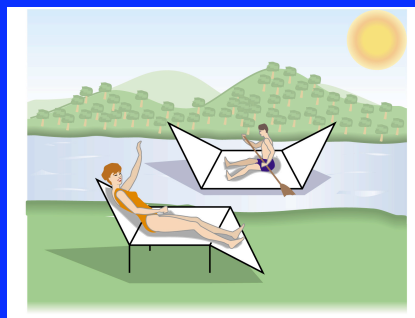
• The chair conformation of cyclohexane is free of strain

chair conformer of cyclohexane

Newman projection of the chair conformer

ball-and-stick model of the chair conformer of cyclohexane
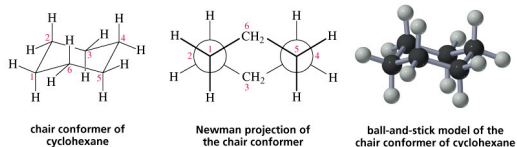
Chair is the most stable conformation of cyclohexane
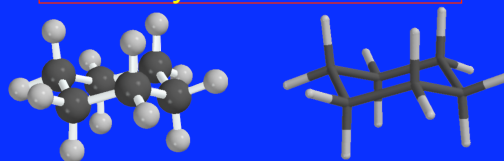
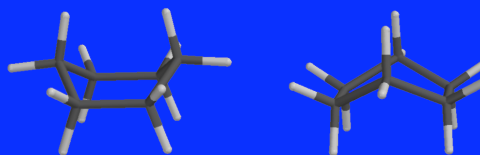

- All of the bonds are staggered and the bond angles at carbon are close to tetrahedral.

Boat conformation is less stable than the chair

180 pm
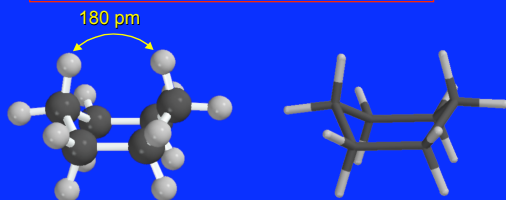
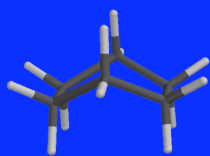- All of the bond angles are close to tetrahedral but close contact between flagpole hydrogens causes strain in boat.

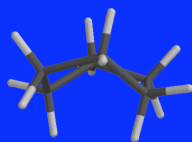## Boat conformation is less stable than the chair

- Eclipsed bonds bonds gives torsional strain to boat.

Skew boat is slightly more stable than boat

Boat   Skew or Twist Boat

- Less van der Waals strain and less torsional strain in skew boat.

Generalization

- The chair conformation of cyclohexane is the most stable conformation and derivatives of cyclohexane almost always exist in the chair conformation

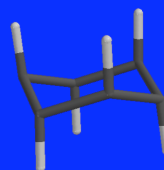## Axial and Equatorial Bonds in Cyclohexane

Drawing Cyclohexane

axial bond

equatorial bond

▲ = axial bond
● = equatorial bond
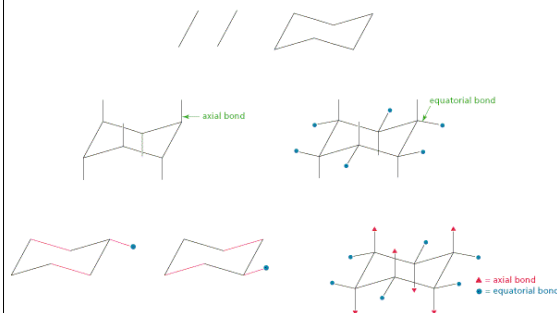
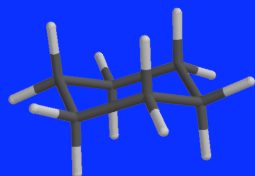## The 12 bonds to the ring can be divided into two sets of 6.
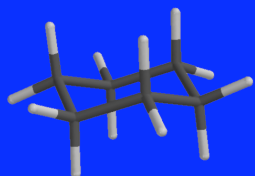
6 Bonds are axial

Axial bonds point "north and south"

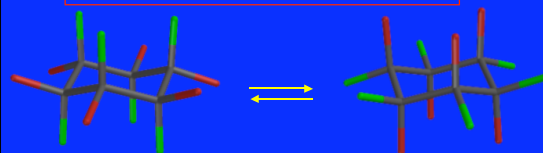The 12 bonds to the ring can be divided into two sets of 6.
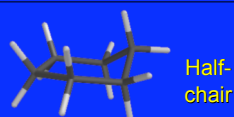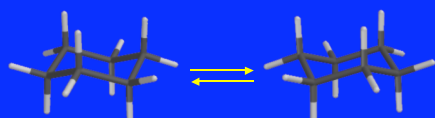

6 Bonds are equatorial

Equatorial bonds lie along the equator

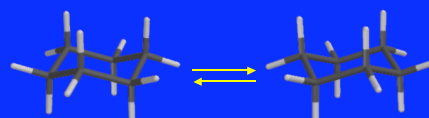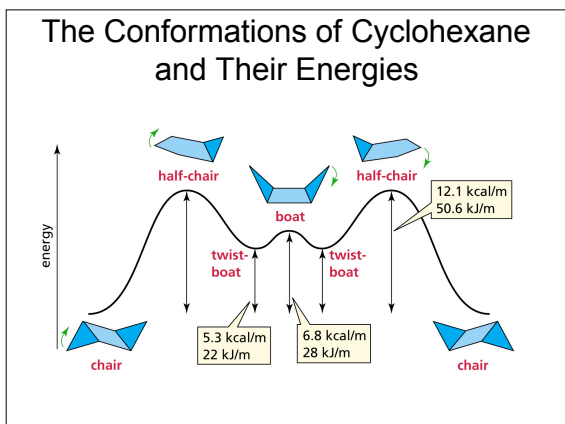*Conformational Inversion (Ring-Flipping) in Cyclohexane*

Conformational Inversion

- chair-chair interconversion (ring-flipping)
- rapid process (activation energy = 45 kJ/mol)
- *all axial bonds become equatorial and vice versa*

Half-chair

The Conformations of Cyclohexane and Their Energies
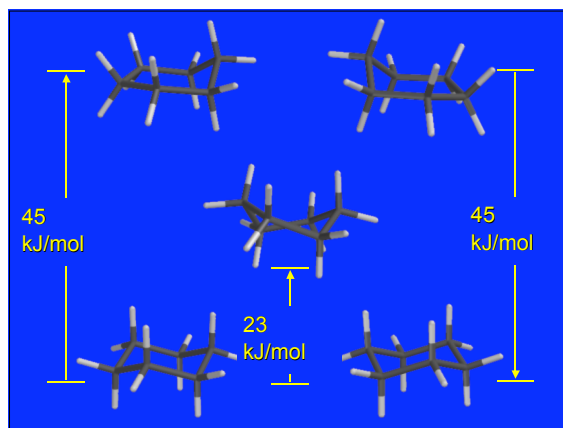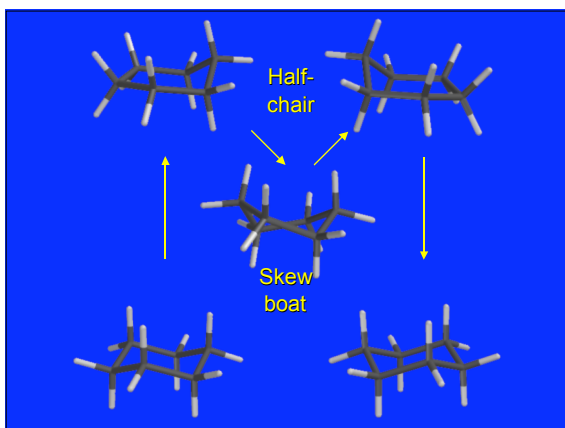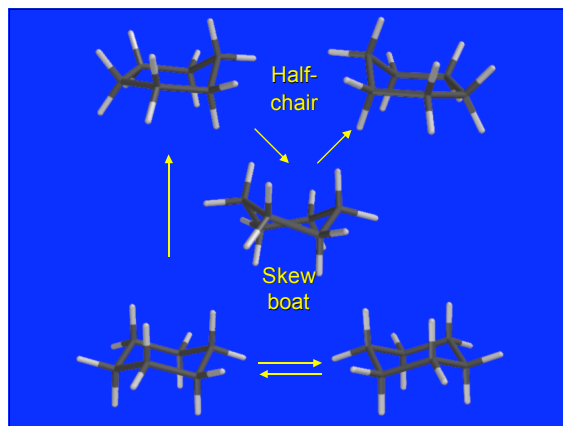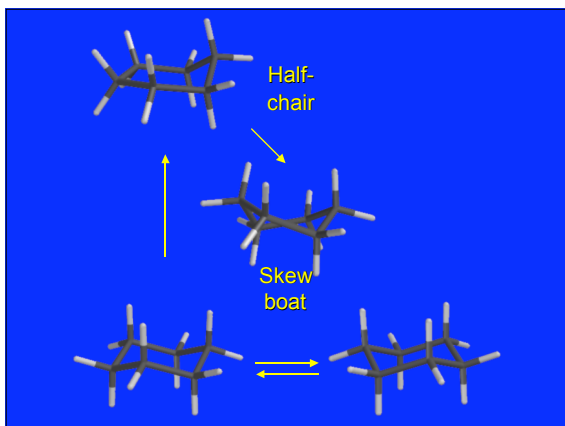
Question 3.5

- Rank the conformations of cyclohexane in order of decreasing stability.

- A) chair > half-chair > twist-boat
- B) chair > twist-boat > half-chair
- C) twist-boat > half-chair > chair
- D) half-chair > twist-boat > chair

Conformational Analysis of Monosubstituted Cyclohexanes
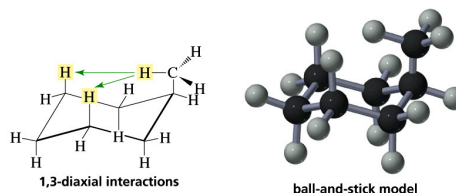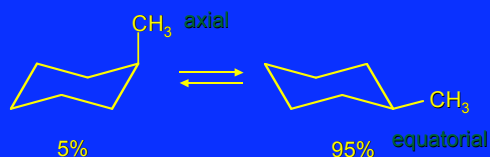
- most stable conformation is chair
- substituent is more stable when equatorial

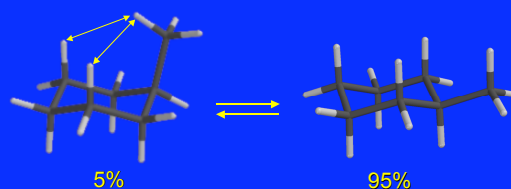## Steric Strain of 1,3-Diaxial Interaction in Methylcyclohexane

1,3-diaxial interactions

ball-and-stick model

Methylcyclohexane

CH_3 axial

CH_3 equatorial

5%   95%

- Chair chair interconversion occurs, but at any instant 95% of the molecules have their methyl group equatorial.
- An axial methyl group is more crowded than an equatorial one.

Methylcyclohexane

5%   95%

- Hydrogen atoms closer than 2.4 Angstroms will cause steric strain.
- This is called a "1,3-diaxial repulsion" a type of van der Waals strain or Steric strain.

Fluorocyclohexane

F

F

40%   60%
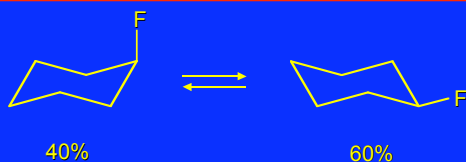
- Crowding is less pronounced with a "small" substituent such as fluorine.
- Size of substituent is related to its branching.

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tert-Butylcyclohexane

$C(CH_3)_3$

$C(CH_3)_3$

Less than 0.01%   Greater than 99.99%
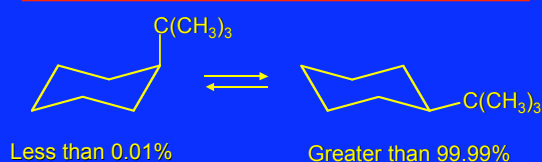
- Crowding is more pronounced with a "bulky" substituent such as tert-butyl.
- tert-Butyl is highly branched.

tert-Butylcyclohexane

van der Waals strain due to 1,3-diaxial repulsions

- The larger the substituent on a cyclohexane ring, the more the equatorial substituted conformer will be favored

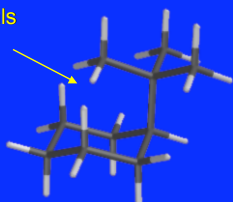| Table 2.10	Equilibrium Constants for Several Monosubstituted Cyclohexanes at 25 °C					
Substituent	Axial $\xrightleftharpoons{K_{eq}}$ Equatorial			Substituent	Axial $\xrightleftharpoons{K_{eq}}$ Equatorial	
H	1			CN		1.4
CH_3	18			F		1.5
CH_3CH_2	21			Cl		2.4
$CH_3\overset{CH_3}{\underset{}{CH}}$	35			Br		2.2
				I		2.2
$CH_3\overset{CH_3}{\underset{CH_3}{C}}$	4800			HO		5.4

K_{eq} = [equatorial conformer]/[axial conformer]

Disubstituted Cyclohexanes Cis-trans Isomerism

Cyclic Alkanes Stereochemistry
Cis -Trans Isomers

cis-2-butene

trans-2-butene

cis-1,2-dimethylcyclopentane

trans-1,2-dimethylcyclopentane
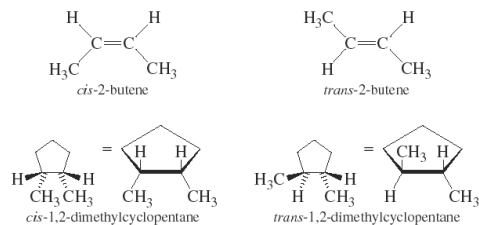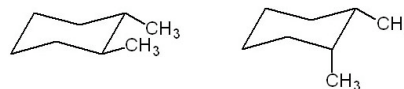

Question 3.6

- What is the relationship between the two chair conformations below?

- A)   conformational isomers
- B)   constitutional isomers
- C)   different compounds
- D)   stereoisomers
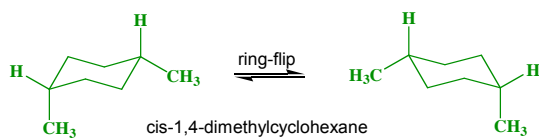

Question 3.7

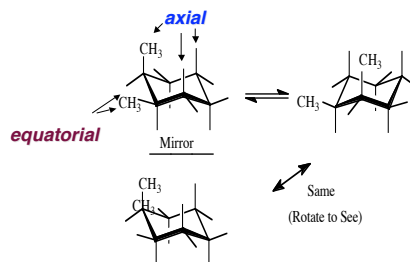- What is the relationship between the two cyclohexane chairs below?

- A)   conformational isomers
- B)   constitutional isomers
- C)   stereoisomers
- D)   different compounds

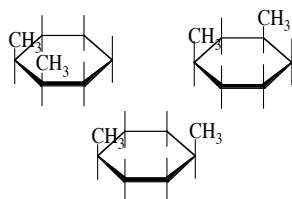## The Chair Conformers of *cis*-1,4-Dimethylcyclohexane

cis-1,4-dimethylcyclohexane

## 1,2-disubstituted-**cis**-cyclohexane Stereochemistry

Cyclohexane Stereochemistry
Drawings: Cis isomers & the need for perspective

Are the methyl groups axial or equatorial?
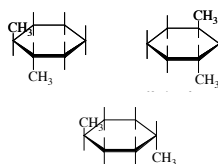*What is the actual conformational shape of the cyclohexane ring?*

The Chair Conformers of *trans*-1,4-Dimethylcyclohexane

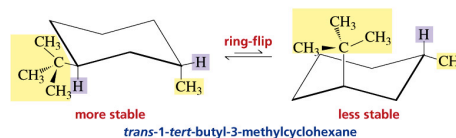trans-1,4-dimethylcyclohexane

This chair conformer has
four 1,3-diaxial interactions.
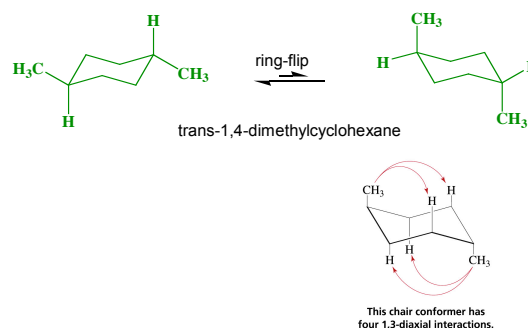
Cyclohexane Stereochemistry
Trans isomers

1-*tert*-Butyl-3-Methylcyclohexane

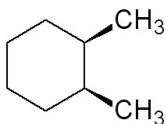more stable   less stable
trans-1-*tert*-butyl-3-methylcyclohexane

Question 3.8

- Which of the listed terms best describes the relationship between the methyl groups in the chair conformation of the substance shown?
-    A)   eclipsed
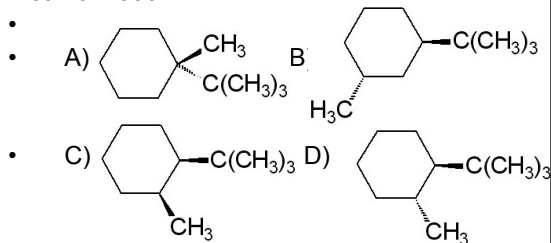-   B)   trans
-    C)   anti
-    D)   gauche

Question 3.9

- Which of the following statements best describes the most stable conformation of
-    *trans*-1,3-dimethylcyclohexane?
-    A)   Both methyl groups are axial.
-    B)   Both methyl groups are equatorial.
-    C)   One methyl groups is axial, the other   equatorial.
-    D)   The molecule is severely strained and   cannot exist.

Question 3.10

- Which of the following has an equatorial methyl group in its most stable conformation?
-
-    A)   B)
-    C)   D)

Question: *Cyclohexane Stereochemistry*

Complete the Table: Cis -Trans Isomers: a = axial; e = equatorial

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

A) cis=*e,a*; trans= *a,e*   **B)** cis = *e,a*; trans= *a,e*   **C)** cis=*e,e*; trans= *a,e*

Question 3.11

trans-1-isopropyl-3-methylcyclohexane is:

-    A)   B)
-    C)   D)

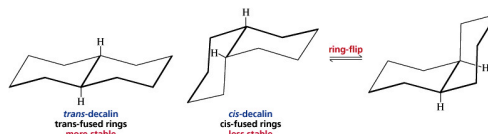 1) A   2) B   3) B & D   4) A & C

Question 3.12

- The most stable conformation of *cis*-1-tert-butyl-4-methylcyclohexane has
-    A)   both groups equatorial
-    B)   both groups axial
-    C)   the *tert*-butyl group axial and the methyl   equatorial
-    D)   the *tert*-butyl group equatorial and the   methyl axial

Question 3.13

- The most stable conformation of the compound to the right has

CH$_2$CH$_3$

- A) an axial methyl group
- an axial ethyl group.
- B) an axial methyl group
- an equatorial ethyl group
- C) an equatorial methyl group and an equatorial ethyl group.
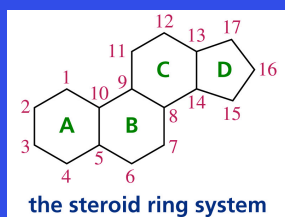- D) an equatorial methyl group and an axial ethyl group.

C(CH$_3$)$_3$

CH$_3$
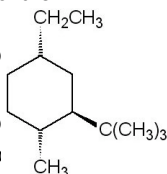
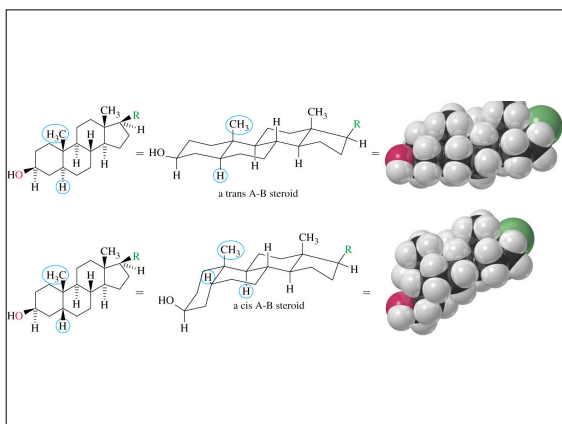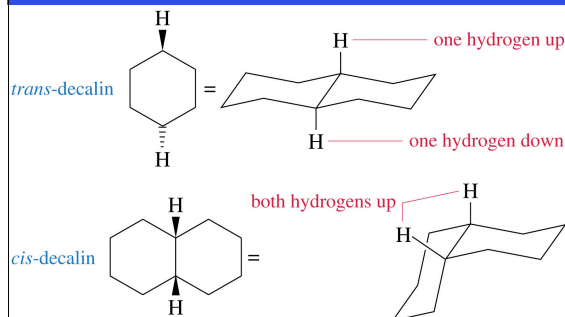## Conformations of Fused Rings

trans-decalin
trans-fused rings
more stable

cis-decalin
cis-fused rings
less stable

ring-flip

- Trans-fused cyclohexane ring is more stable than cis-fused cyclohexane ring

Steroids

the steroid ring system

Steroid A/B and B/C Rings Resemble Decalin

trans-decalin

one hydrogen up

one hydrogen down

cis-decalin

both hydrogens up

a trans A-B steroid

a cis A-B steroid

Steroid B/ C, and C/D rings are trans fused

angular methyl groups

CH$_3$ and H are trans

CH$_3$ and H are cis
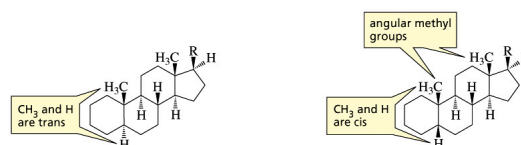
Methyl groups at C-10 and C-13 are "angular" methyl groups

Question 3.14

- The structure shown is the carbon skeleton of adamantane, a hydrocarbon having a
- structure that is a section of the diamond lattice. Adamantane is:
- A) bicyclic
- B) tricyclic
- C) tetracyclic
- D) pentacyclic