

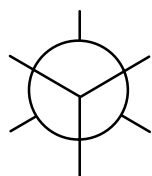
Chapter 4: Stereochemistry of Alkanes and Cycloalkanes

Stereochemistry deals with the 3D aspects of molecules.

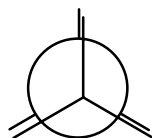
Conformational isomers can be shown using Newman Projections or Sawhorses.

Newman Projections

The circle in the Newman projection represents the carbon-carbon bond, viewed one carbon in front of the other. Bonds attached to the front carbon are shown by lines going to the center of the circle. Bonds attached to the rear carbon are shown by lines going to the edge of the circle.



Staggered



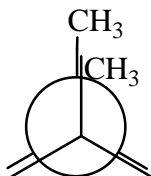
Eclipsed

Rotation around the carbon-carbon bond alternates between staggered and eclipsed.

Newman Projections show the relationships (angles) between the substituents.

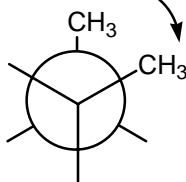
Eclipsed

Conformation of butane (2 methyl groups are eclipsed. Circle represents the C2-C3 bond of butane)

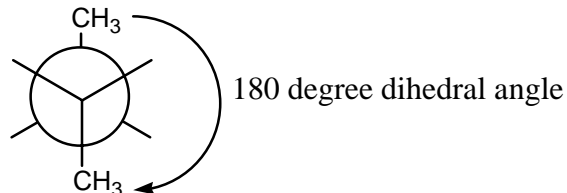


Staggered (Gauche)

60 degree dihedral angle



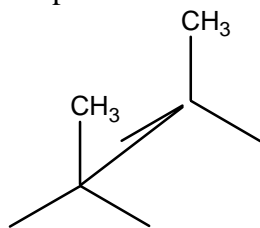
Staggered (Anti)



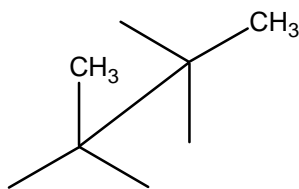
Sawhorses

Increasing Stability

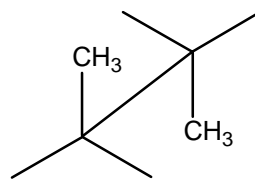
Eclipsed



Gauche



Anti



Strain and Stability

Torsional Strain

Strain on a molecule caused by bond opposition, electron repulsion between eclipsing bonds.

Steric Strain

Repulsion between atoms and groups

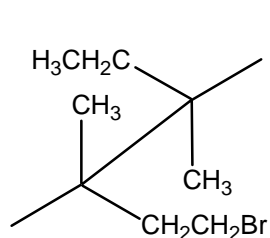
The higher the strain, the less stable the conformation

Eclipsed conformations are less stable than staggered conformations. Why? The main reason is that torsional strain is high in eclipsed conformations. The bonds on the front and back carbons are close to each other and repel each other destabilizing the molecule.

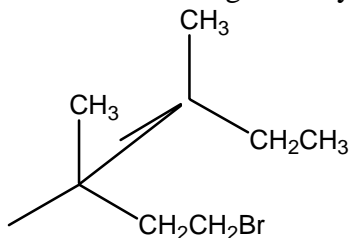
Of the staggered conformations, groups that are gauche to each other (60 degree dihedral angle) are less stable than when they are anti to each other (180 degree dihedral angle). Why? Groups in a gauche position have higher steric strain because the groups are closer to each other. Therefore, they repel each other more than in the anti position.

Practice Problem

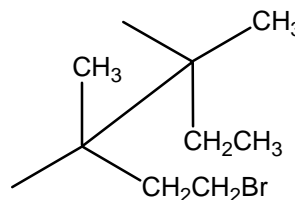
1. Rank the following in order of increasing stability:



A



B



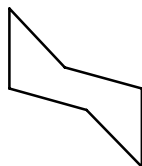
C

Answer

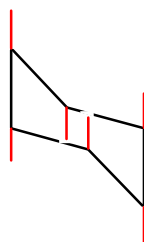
Conformations of Cyclohexane

Cyclohexane moves into a 3-D conformation, called a chair conformation, that relieves both torsional and ring strain.

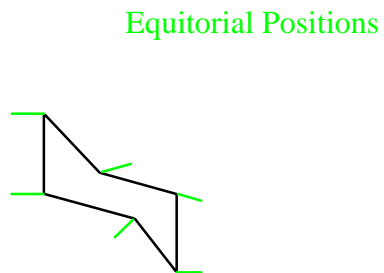
Cyclohexane Chair



Axial and Equatorial bonds in Cyclohexane

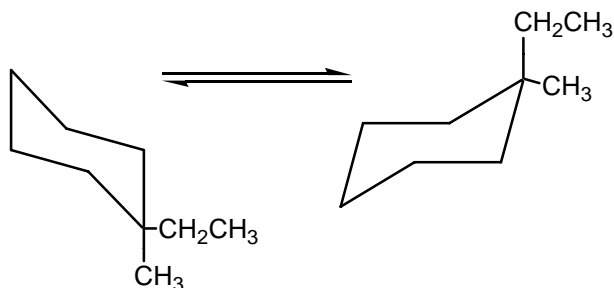


Axial Positions



Equatorial Positions

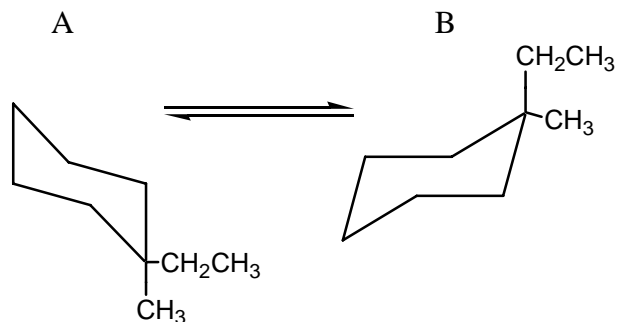
Notice that axial positions and equatorial positions alternate their up or down orientation. Rings can flip so that substituents in the axial position move to the equatorial position and vice versa. However, during this flip, the general up or down direction is retained. This means that axial up flips to become equatorial up. Equatorial down flips to become axial down.



Substituents in the equatorial position contribute less steric strain to the molecule. Substituents in the axial position contribute more steric strain to the molecule. Therefore, the conformation with the bigger groups in the equatorial position is more stable.

Practice Problems

2. Which is the most stable conformation?



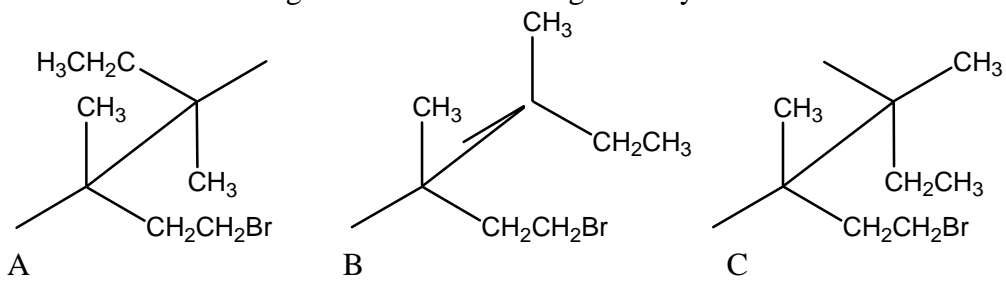
Answer

3. Is *cis*- or *trans*- 1,3-disubstituted cyclohexane more stable? Why?

Answer

Answer

1. Rank the following in order of increasing stability:



B-eclipsed- always less stable than staggered.

A-Staggered-2 sets of gauche and 2 sets of anti interactions

C-staggered-3 sets of gauche and 1 set of anti interactions.



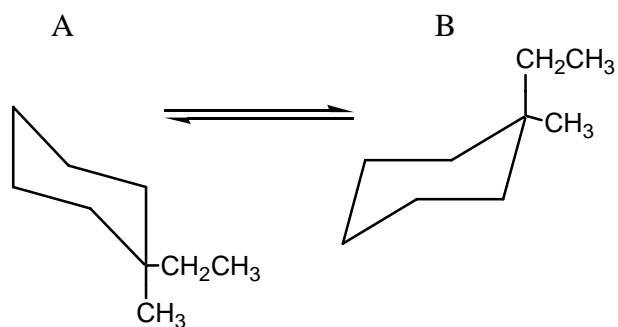
Least stable

Most stable

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Answer

2. Which is the most stable conformation?



Both A and B have one substituent in the axial position and one substituent in the equatorial position. Since the ethyl group is bigger than the methyl group, the conformation with ethyl in the equatorial position is most stable. A is more stable, and the equilibrium mixture of the two contains more A than B.

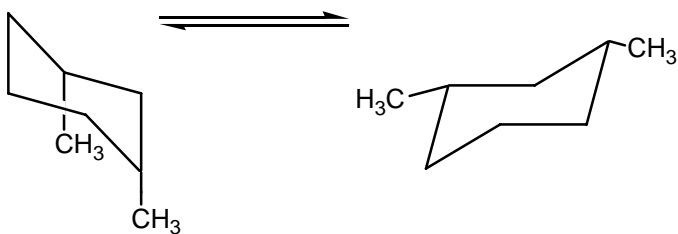
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Answer

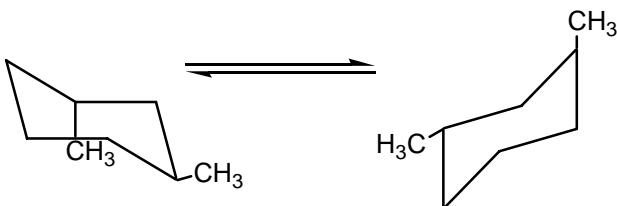
3. Is *cis*- or *trans*- 1,3-disubstituted cyclohexane more stable? Why?

Cis and *Trans* can each exist in two forms:

Cis



Trans



In cis-1,3-disubstituted cyclohexane, both substituents exist in either the equatorial position or axial position. The equilibrium strongly favors the diequatorial form.

In trans-1,3-disubstituted cyclohexane, one substituent is in the equatorial position and one is in the axial position.

Therefore, the *cis*-isomer, which exists almost exclusively in the diequatorial conformation, is more stable than the axial-equatorial *trans* isomer.

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