ORGANIC CHEMISTRY 1 LECTURE GUIDE 2019

BY RHETT C. SMITH

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Organic Chemistry 1
Lecture Guide 2019

By Rhett C. Smith, Ph.D.

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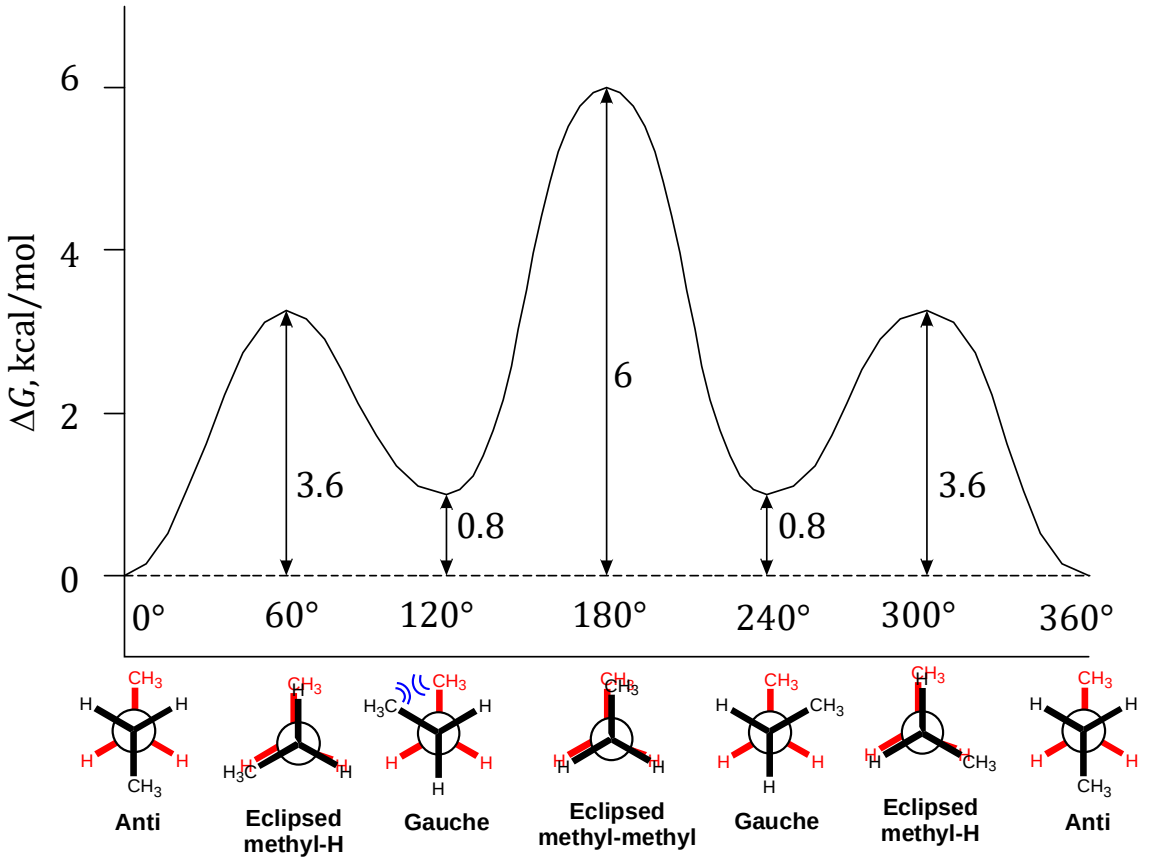
Companion Books from the Proton Guru:

Organic Chemistry 1 Reactions and Practice Problems 2019

by Rhett C. Smith

Organic Chemistry 1 Primer 2019,

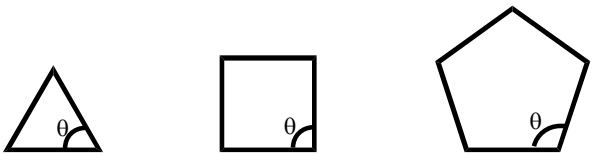
by Rhett C. Smith, Andrew G. Tennyson, and Tania Houjeiry


6
4
2
0
ΔG, kcal/mol
3.6
0.8
6
0.8
3.6
0°
60°
120°
180°
240°
300°
360°
Anti
Eclipsed methyl-H
Gauche
Eclipsed methyl-methyl
Gauche
Eclipsed methyl-H
Anti

Notes

We have discussed steric strain (including torsional strain) in linear alkanes.

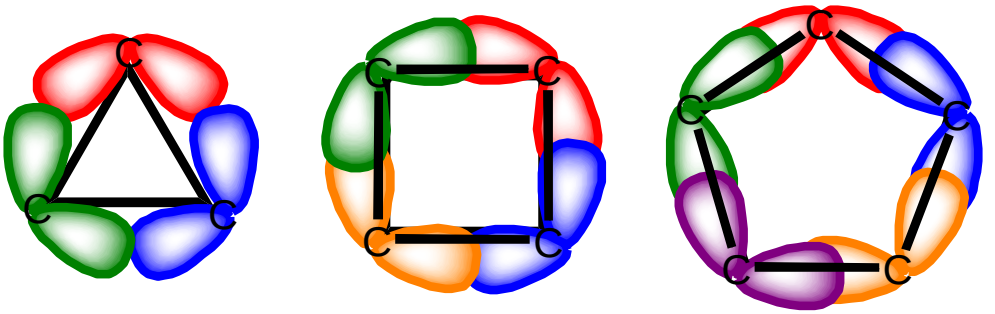
One additional consideration for cyclic compounds is **angle strain**. Cycloalkanes are made of sp^3 hybridized carbons, which favor bond angles of 109.5°. However, this differs from the angles in some regular polygons:



θ = 60° θ = 90° θ = 108°

The difference between ideal and actual angle leads to **angle strain**. We consider this as part of the overall **Ring strain:**

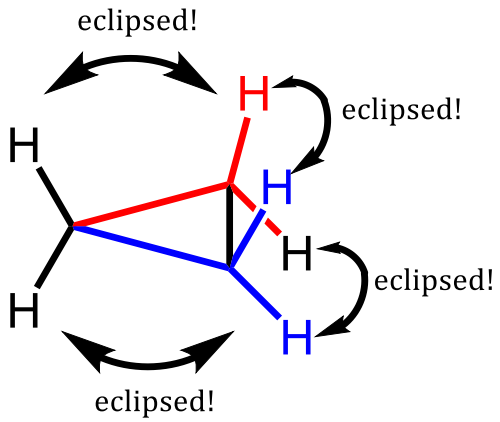
Notes

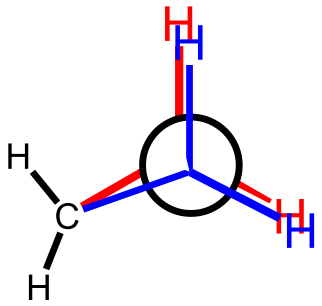


An **origin of angle strain**

Now we consider the other contributors to ring strain: steric interactions (and torsional strain)

Notes

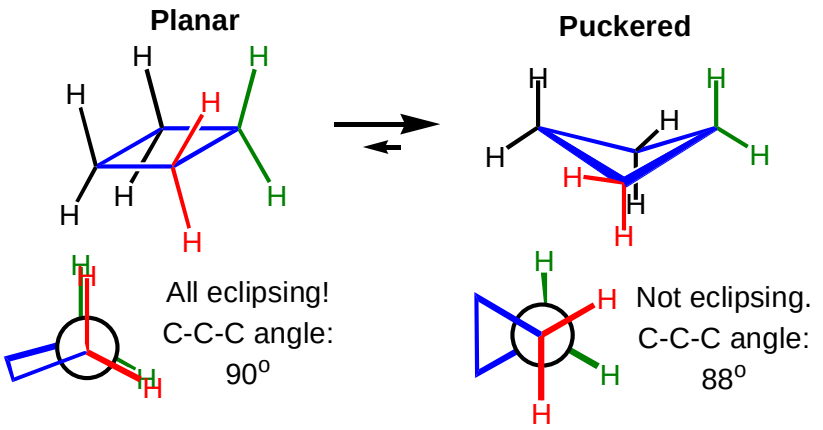




In addition to lots of **angle strain**, cyclopropane also has

The total **ring strain** is about 30 kcal/mol (10 kcal per methylene).

Notes

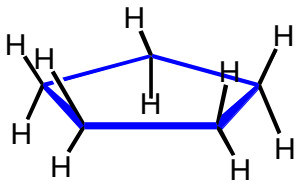


In addition to **angle strain**, planar cyclobutane has H's eclipsed. **Molecules will always**

Cyclobutane twists ("puckers"), increasing the angle strain a bit, but relieving all of the eclipsing torsional strain. The puckered form, on the right, is the favored form. The total **ring strain** is about 28 kcal/mol (7 kcal per methylene).

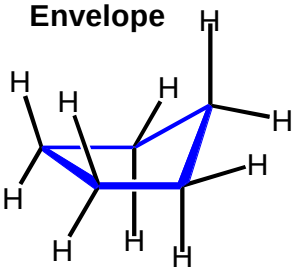
Notes

Planar



All eclipsing!

Envelope



relieves some eclipsing.

In addition to some **angle strain**, planar cyclopentane also has

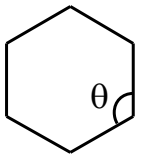
(A)

Cyclopentane undergoes a distortion to the **envelope form**, relieving some of the eclipsing torsional strain, so:

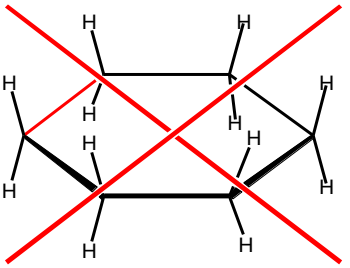
(B)

The total **ring strain** is about 10 kcal/mol (2 kcal per methylene).

Notes



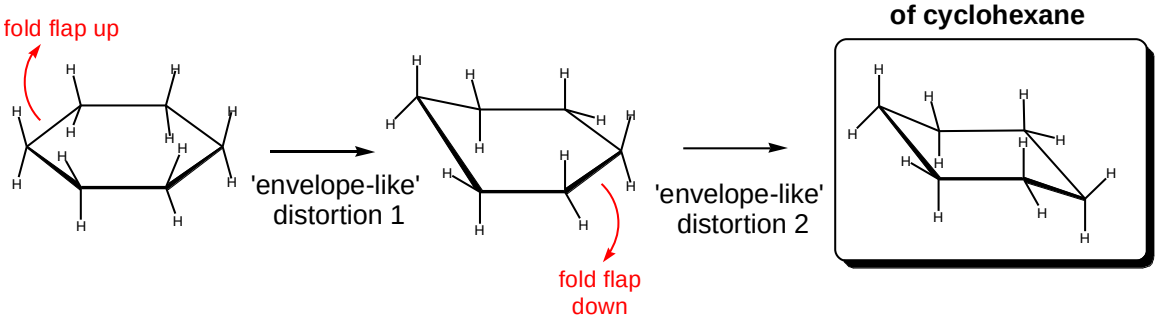
θ = 120°



Planar: ring strain from:

A

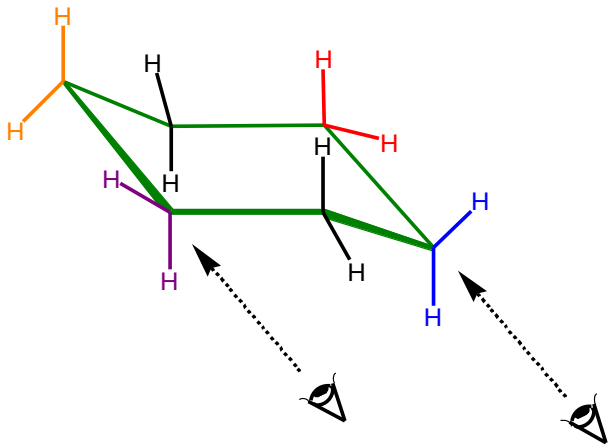
Chair conformation of cyclohexane



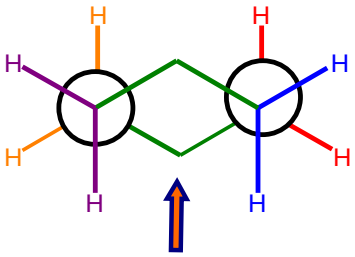
Ring strain in the Chair Conformation:

We will now study why this is the case.

Notes



All staggered.



This picture shows two Newman Projections; one projection down the right side and one down the left side of cyclohexane (indicated by the eyes). Build a model to see this more easily.

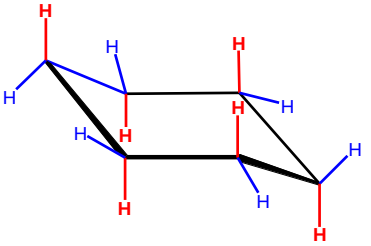
The chair conformation features
1.

2.

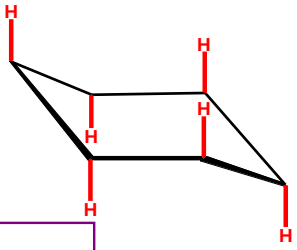
This is **why the chair conformation is very stable**.

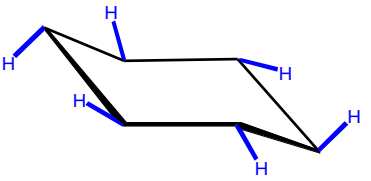
Notes

There are two distinct types of hydrogen atoms in cyclohexane. It is very important to understand the difference between these two types.



Note: Each C has one equatorial and one axial H and each type alternates up and down around the ring.

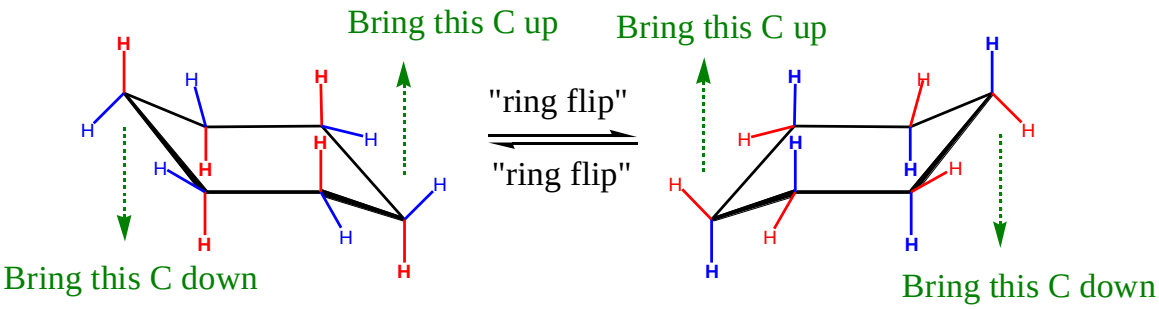




: 'stick straight up and down'. If you build a model of the chair conformation of cyclohexane these are the atoms that it will 'stand on.'

: point up and down at an angle around the <u>equator</u> of the cyclohexane.

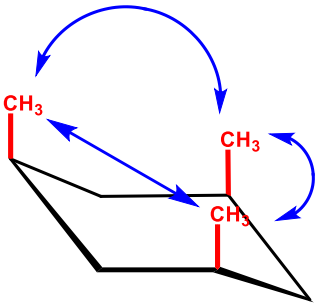
Notes

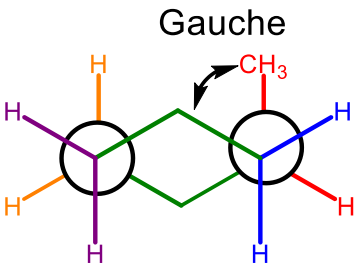


A **ring flip** involves distorting the cyclohexane ring so that the 'up' flap moves to the 'down' position and vice versa.

A **ring flip** switches:

Notes





Substituents may cause steric strains. Axial methyl (or larger) groups can clash with other axial substituents on the same face of the ring. This type of steric interaction is called a

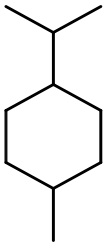
Ⓐ

Equatorial positions do not have these interactions, so

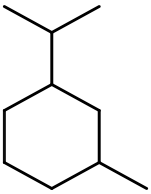
Ⓑ

Notes

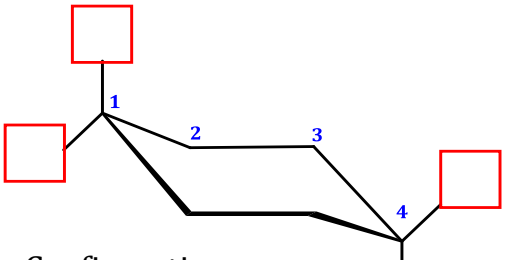
Problem: For each, draw the most stable conformational isomer



1-isopropyl-4-methylcyclohexane

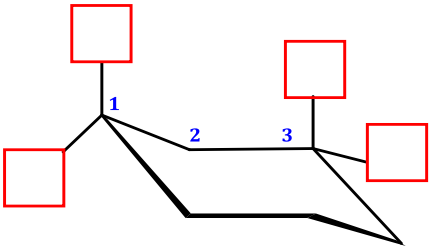


1-isopropyl-3-methylcyclohexane



Configuration:

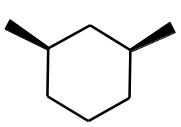
A



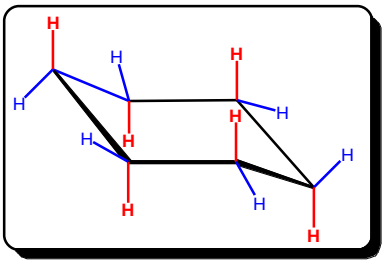
Configuration:

B

Notes



cis-1,3-dimethycyclohexane



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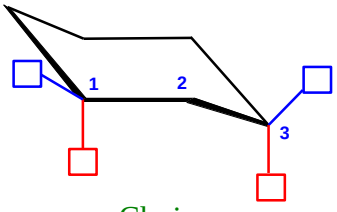
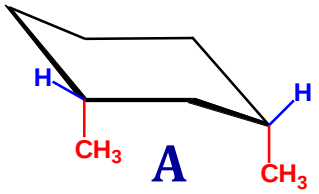
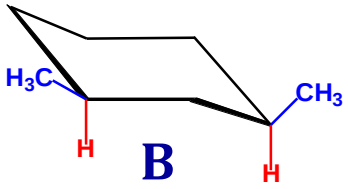
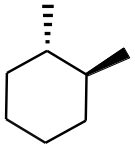


Choices

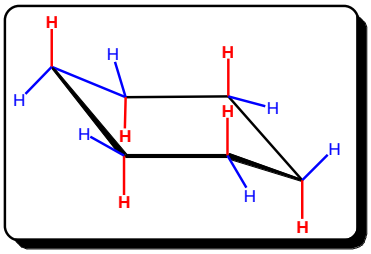




Notes



trans-1,2-dimethycyclohexane



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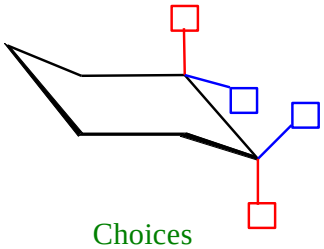


Choices

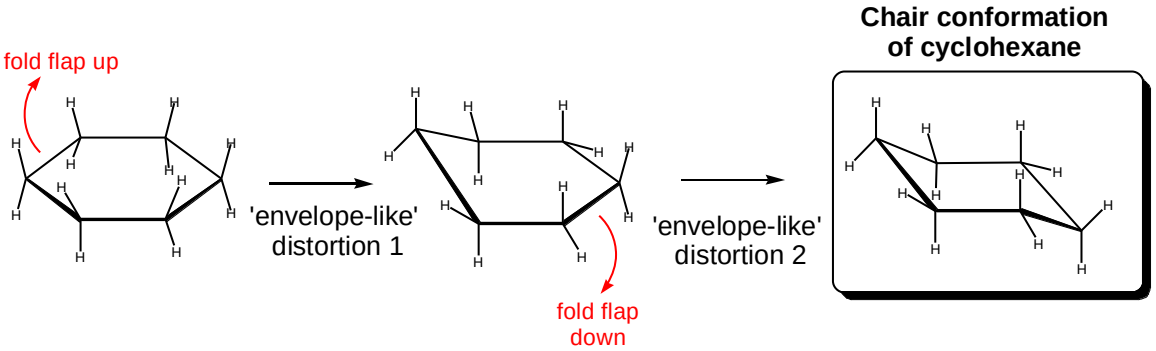
Ⓐ

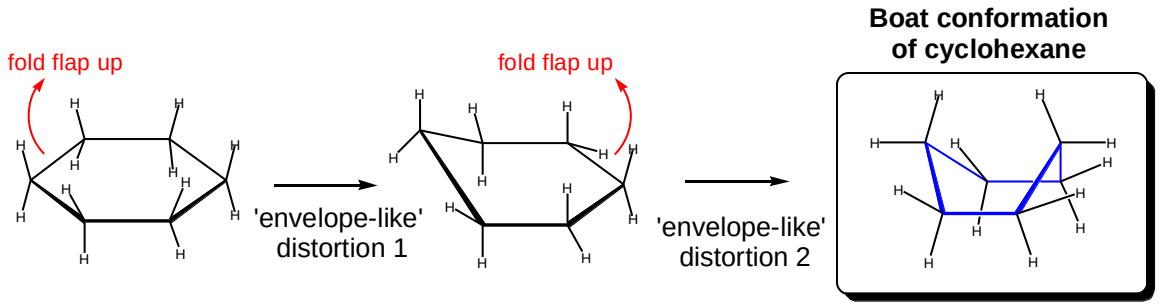
Ⓑ

Axial methyls will have strong 1,3-diaxial repulsion, so this form will be unfavorable. The most stable form is therefore:

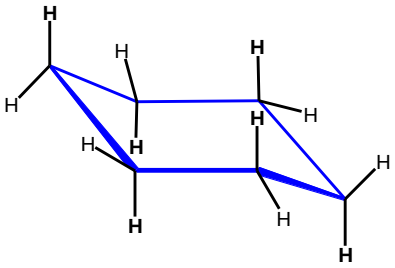
Ⓒ

Notes

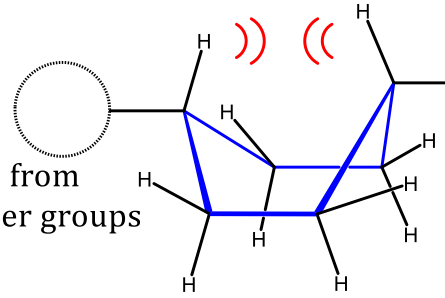

fold flap up
'envelope-like' distortion 1
fold flap down
'envelope-like' distortion 2
Chair conformation of cyclohexane


fold flap up
fold flap up
'envelope-like' distortion 1
'envelope-like' distortion 2
Boat conformation of cyclohexane

Notes



Steric interaction
(known as a **"flagpole" interaction**)



Far from other groups

Far from other groups

"**chair**" conformation is very stable:
- no eclipsing interactions
- angles favorable
- Generally preferred

"**boat**" conformation
- eclipsing interactions
- steric strain
-angles strained

Boat only preferred when:

Notes