Alkanes

4 - Conformations

Dr. Sapna Gupta

Conformation - Introduction

Conformation is different representation of molecules due to rotation of single bonds. No bonds are broken, only rotated. The different isomers obtained from this rotation are called “conformers”.

All sp^3 bonds in straight chain alkanes can rotate but in cycloalkanes rotation is not possible because the bonds will break (hence the cis and trans isomers possible). We will cover aliphatic, straight chain, alkanes first.

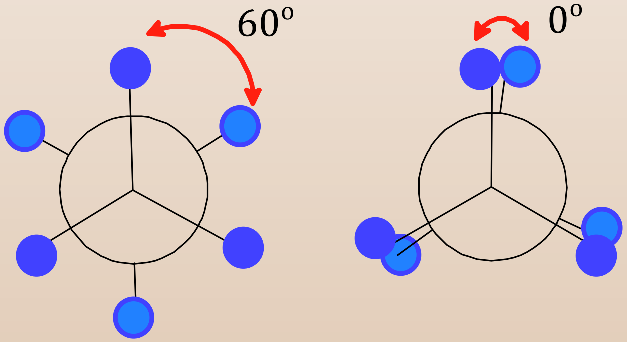
In both aliphatic and cyclo- alkanes we look at the 3D relationship of two carbons at a time. How close are the groups to each other? At what angle are the groups to each other? What are the sizes of the groups? And do they have an effect on each other? These terms are used for both straight chain and cyclic alkanes.

To understand this, we need to first learn some terminology of this topic.

Conformations - Terminology

The terms below are commonly used to express what the molecule will look like in a three-dimension space.

- **<u>Dihedral angle</u> *θ***: (Greek theta): The angle created by two intersecting planes. In eclipsed state, where the angle is 0º, groups or atoms are spatially closer to each other. When the angle is higher, then the groups are spatially farther away.



- **<u>Steric strain</u>**: The strain that arises when atoms or groups on adjacent or nearby atoms are large and cause "crowdedness" in the space. This forces atoms to be closer to each other than their atomic (contact) radii will allow.
- **<u>Angle strain</u>**: Strain that arises when a bond angle is either compressed or expanded compared to its optimal value. Optimum value is determined by the atom's hybridization.

Watch the video (Conf Video 1) explaining all these terms. See the link in the "Description".

Conformations of Ethane

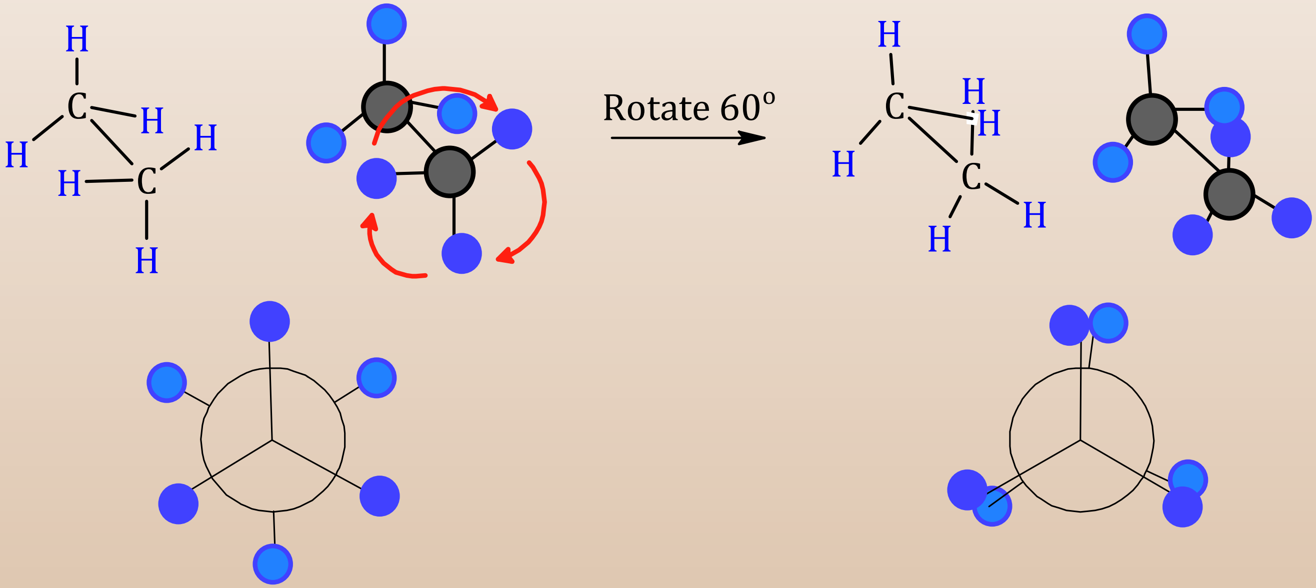
Ethane is a simple alkane of two carbons, but because of bond rotation it can have different conformations.

There are two different ways to show the 3D structure of an aliphatic alkane on paper: Fisher (sawhorse) projection and Newman projections. I have colored the hydrogens on the back carbon just a little lighter blue so you can visualize the front and back hydrogens. The Fisher projections are shown in C-H structure and ball stick model. Newman projection is the where the back carbon is shown as a circle.

See the next slide for the conformations of ethane.

Conformations of Ethane - Contd

In ethane there is not much energy differences since hydrogens are small atoms and do not create much steric or angle strain.



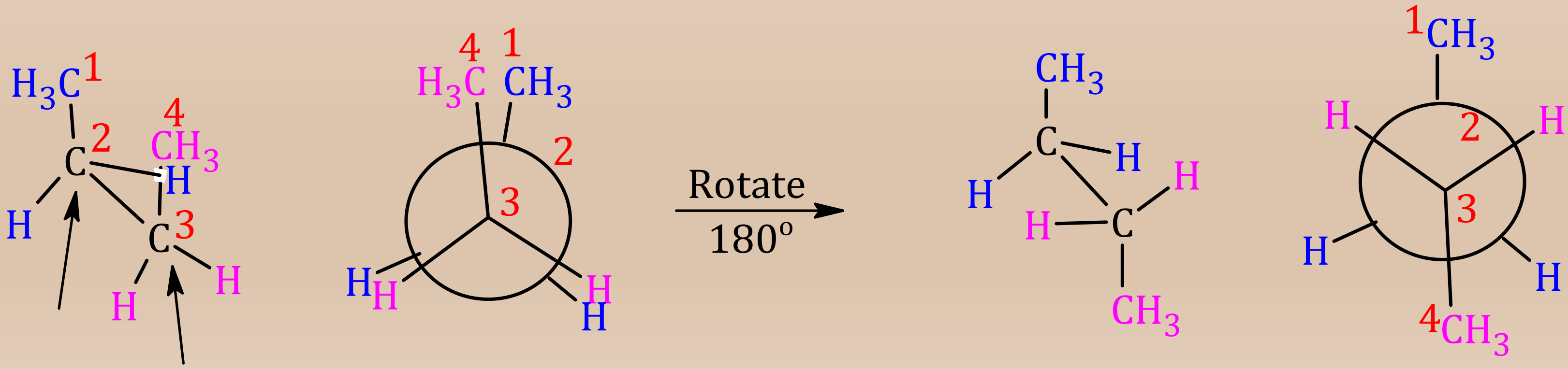
Watch the video (Conf Video 2) for conformations of ethane. See the link in the "Description".

Conformations of Butane

Butane, an alkane of four carbons, has more atoms and thus can have different conformations.

Below are the two conformations of butane, the Fisher and Newman. The atoms/groups in blue are on carbon #2 and the pink atoms/groups are on carbon #3, in the front for better visualization. We will focus on carbons 2 and 3 since the interactions between carbons 1 and 2, and carbons 3 and 4 are the same and are don’t have much energy differences because carbons 1 and 4 have hydrogens which are not large atoms thus not presenting much steric tension.

The energy of butane as a function of the dihedral angle about the bond between carbons 2 and 3.



Conformations of Butane - All

It is much easier to use the Newman, rather than Fisher projection, when writing conformations. Newman projections focus on the two carbons we are studying to see the conformers. It is easier to see the dihedral angle between the big groups as well as the steric relationship between them. When we write the conformations, we rotate one carbon, front or back, by 60^o to get the next conformer.

There are three main types of conformers, depending on the dihedral angle between the groups.

Eclipsed: When the dihedral angle is 0^o between groups. The conformer is a true eclipse when the two large groups are right behind each other.

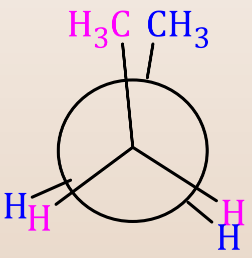
Anti: When the dihedral angle between the two large groups is 180^o. This conformer is lowest in energy because the steric tension is least.

Staggered: This is when the large groups have a 60^o dihedral angle. These can be same or different energy depending on the groups.

See the next slide for all the Newman projections and their descriptions.

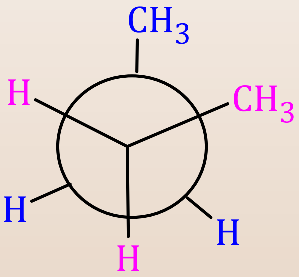
Conformations of Butane - All

There are 6 conformers (360°/60° rotations). Below are the six conformers for butane



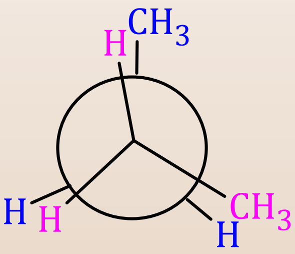
I

Eclipsed



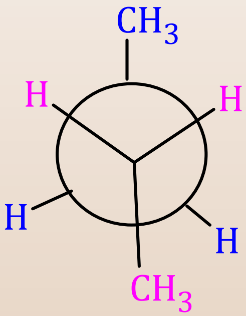
II

Staggered



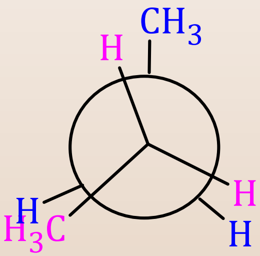
III

Eclipsed



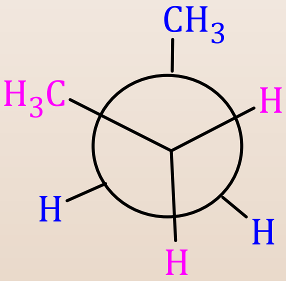
IV

Anti



V

Eclipsed



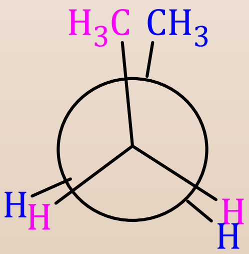
VI

Staggered

Structure I is eclipsed, highest energy. Structure IV is the anti, lowest energy, where the large groups are opposite each other. Structures II and VI are the same called staggered. They have the same energy. Structures III and V are also referred to as eclipse and have the same energy. In the case of butane, structures III and V are not true eclipsed since the large groups are not behind each other.

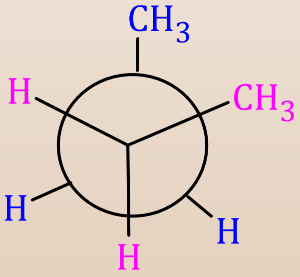
Conformations of Butane - All

NOTE: You can start drawing the conformers with anti first and then write the 6 conformers. You will see that I have kept the back carbon static and rotate only the front carbon. I highly recommend you rotate only one carbon, front or back – its your choice.



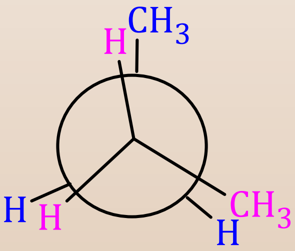
I

Eclipsed



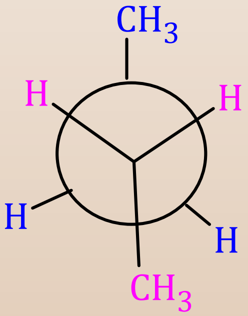
II

Staggered



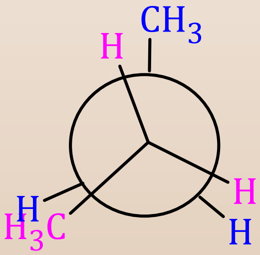
III

Eclipsed



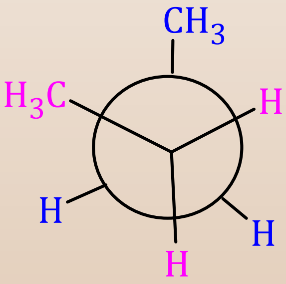
IV

Anti



V

Eclipsed



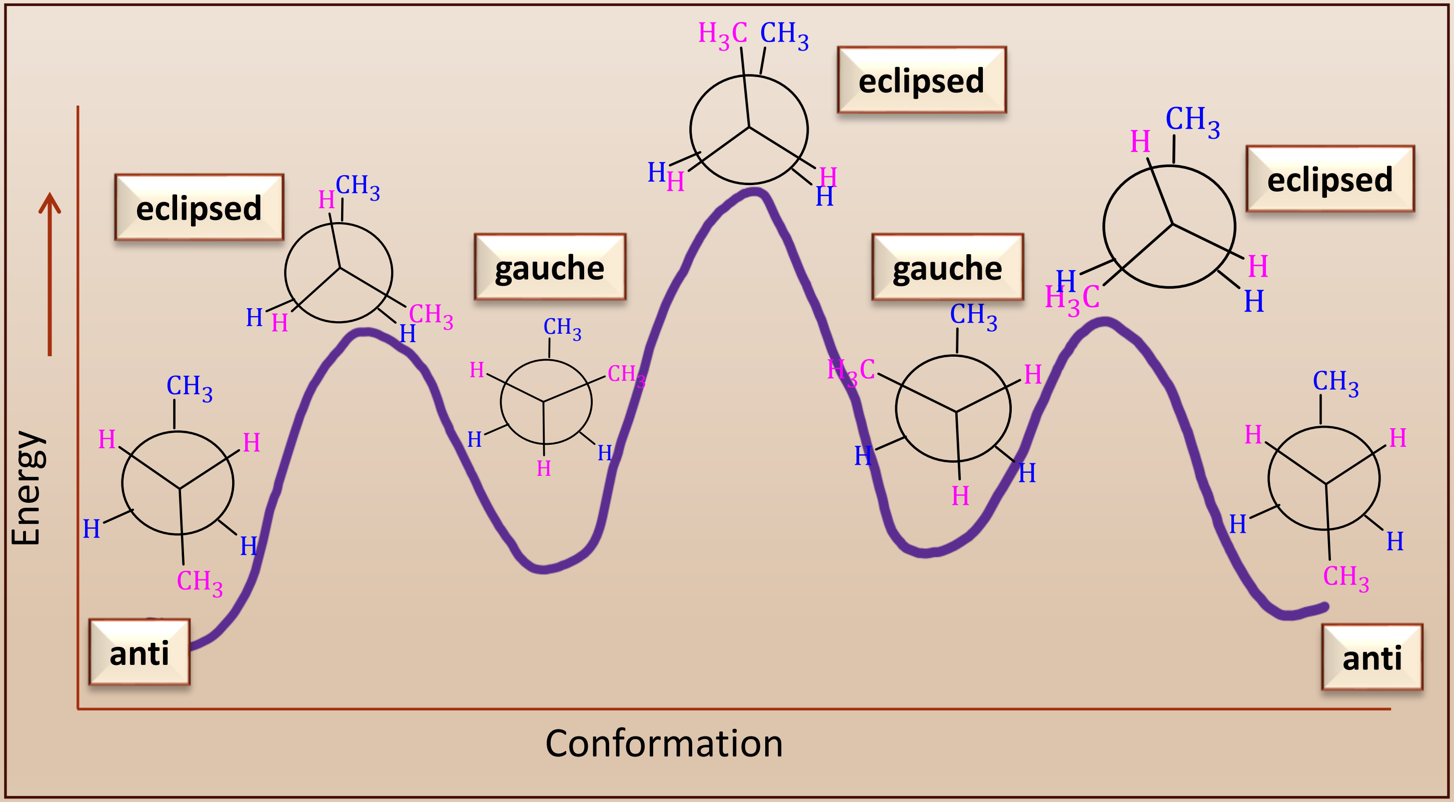
VI

Staggered

Watch the video (Conf Video 3) for conformations of butane. See the link in the "Description".

Energy of Conformations

The graph of the energy of butane as a function of the dihedral angle about the bond between carbons 2 and 3 is sown below. The highest energy is for the eclipse while lowest is for anti.

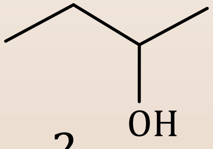


Solved Problem: Writing conformers

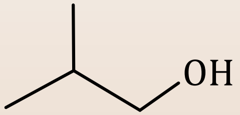
Draw as many compounds as you can that are alcohols with the formula, C_4H_8O. Draw the conformation of one of the constitutional isomers, label them and identify the lowest and highest energy conformers.

ANSWER

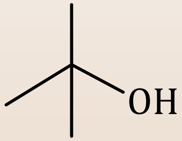
1



2

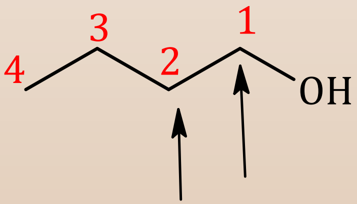


3

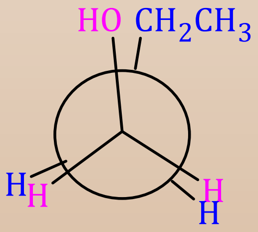


4

Let us write the conformers for isomer 1 focusing on carbons 1 and 2.



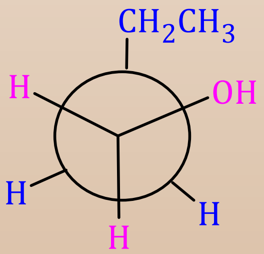
C1 has: OH, H, H
C2 has CH_2CH_3, H, H



I

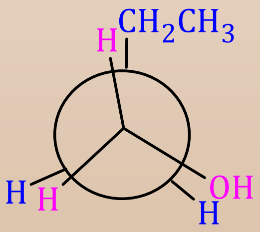
Eclipsed

Highest energy



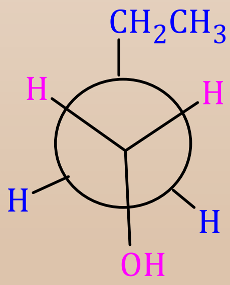
II

Staggered



III

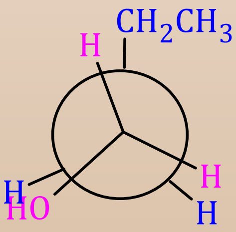
Eclipsed



IV

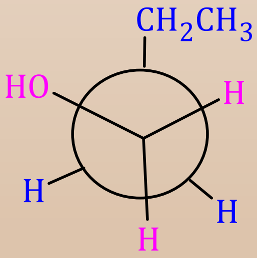
Anti

Lowest energy



V

Eclipsed



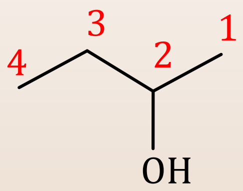
VI

Staggered

Solved Problem: Selecting carbons for writing conformers

Pick any two other structures from the isomers of alcohol, 2-4 and decide which conformers to look at. Write the lowest and highest energy conformers.

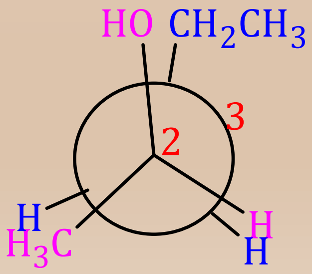
ANSWER

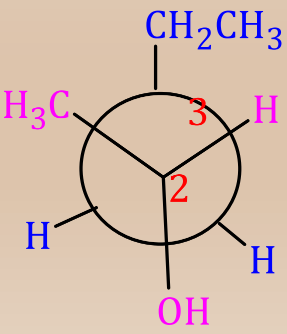


Looking at **C1-C2,** the groups on **C1** are: H, H, H and **C2** has OH, CH_2CH_3, H.
Looking at **C2-C3**, the groups on **C2** are: OH, CH_3, H; **C3** has CH_3, H, H.
Looking at **C3-C4**, the groups on **C3** are $CHOHCH_3$, H, H and **C4** has H, H, H.

The best two conformations to study would be **C2-C3**. The conformers between C1-C2 and C3-C4 will not have much steric tension since C1 and C4 have all hydrogens.
In the two conformers, the highest energy is the eclipse but the lowest energy is not a true anti since the two large groups are staggered, but that is the lowest energy conformer possible.

Highest energy



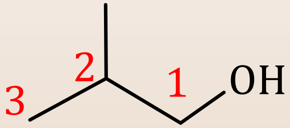


Lowest energy

Solved Problem: Selecting carbons for writing conformers

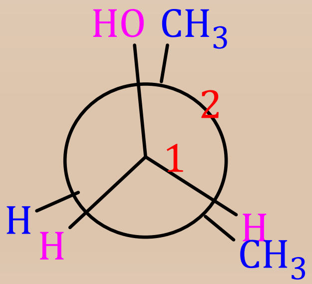
Pick any two other structures from the isomers of alcohol, 2-4 and decide which conformers to look at. Write the lowest and highest energy conformers.

ANSWER

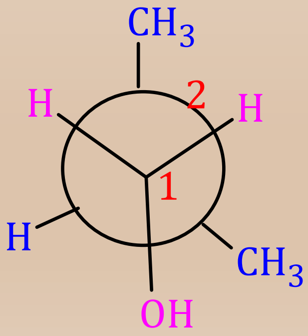


Looking at **C1-C2,** the groups on **C1** are: OH, H, H and **C2** has CH_3, CH_3 , H.
Looking at **C2-C3**, the groups on **C2** are: CH_3, CH_2OH, H and H; **C3** has H, H, H.

The best two conformations to study would be C1-C2. The conformers between C2-C3 will not have much steric tension since C3 has all hydrogens.
In the two conformers, the highest energy is the eclipse but the lowest energy is not a true anti since the two large groups are staggered, but that is the lowest energy conformer possible



Highest energy



Lowest energy

Cycloalkanes - Introduction

Cycloalkanes are ring structures. The smallest ring possible is of three carbons giving a triangle (cyclopropane). As we keep adding one carbon, the ring size increases.

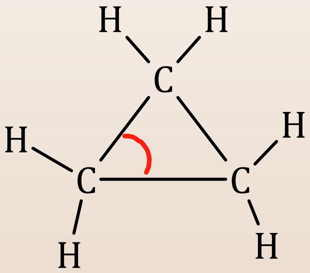
Cycloalkanes are less flexible than open-chain alkanes because they have restricted rotation as we learned during their nomenclature. Because of this restricted rotation they have cis and trans isomers.

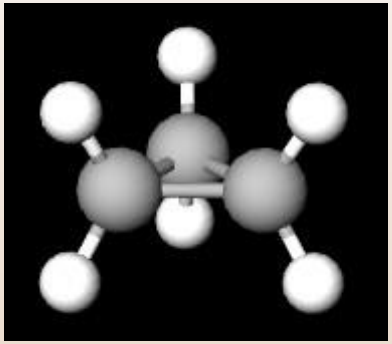
We will use the same terminology as we used for aliphatic conformation here also.

- **Angle strain** is caused by bond angles different from 109.5^o (should be 109^o because in single bond carbons are sp$_3$ hybridized)
- **Tortional strain** is caused by eclipsing C-H bonds on adjacent carbons
- **Steric strain** is due to close proximity of atoms or groups.

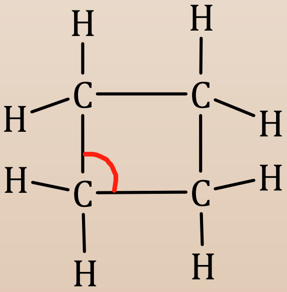
Cyclopropane, Cyclobutane, Cyclopentane

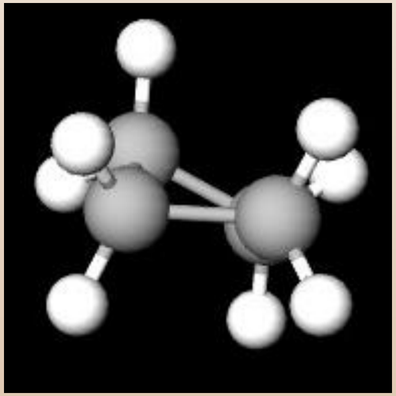
- Cyclopropane has both angle and tortional strain. Cyclopropane is also a planar structure. Bond angle is 60°.



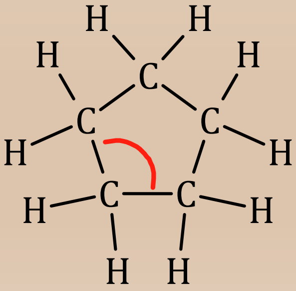


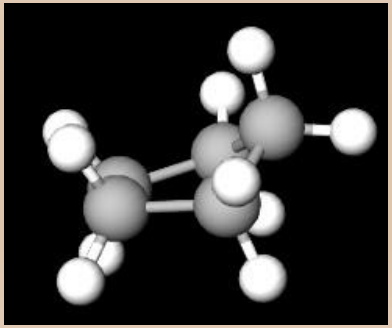
- Cyclobutane has more angle strain. Bond angle is 90°





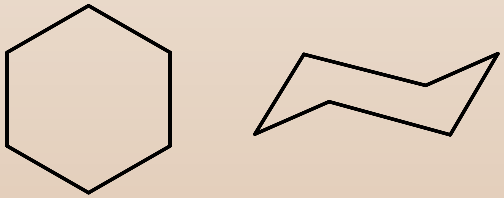
- Cyclopentane is slightly bent (puckered) which reduces the tortional strain. Bond angle is 108°

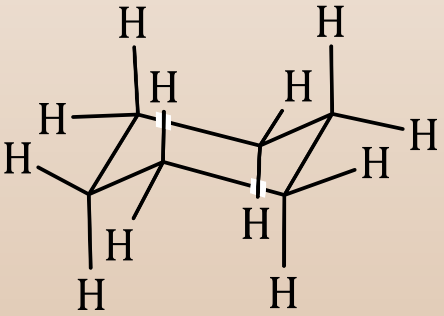


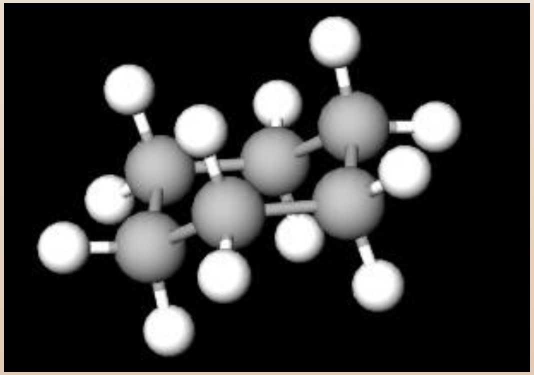


Cyclohexane

Cyclohexane is the most stable ring. Bond angle is 120^{o}. The 3D (ball and stick) model shows the spatial relationship of the hydrogens on each carbon. The first ring structure (hexagon) shows the 2D structure of cyclohexane. The second structure represents the line structure of the 3D model. In cyclohexane, the 2D and 3D models look quite different from each other.







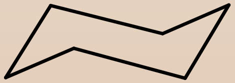
Watch the video (Conf Video 4) to understand ring structures the link in the "Description".

Watch the video (Conf Video 5) to understand cyclohexane in the link in the "Description".

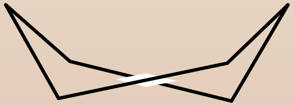
Cyclohexane Conformation

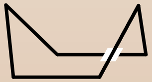
Cyclopropane, cyclobutane and cyclopentane don't have any appreciable conformation structures because they are planar structures. They do have the cis and trans isomers, but those are geometric isomers and not conformers.

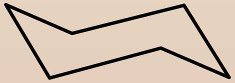
Conformers occur when there is rotation and motion without breaking bonds. The only ring capable of such motion is cyclohexane. The bonds in cyclic compounds cannot rotate but they can still move up or down within certain limits. It has three main conformers, two chairs and a boat. Below are the different ring conformations possible.


chair


boat


twisted boat


boat

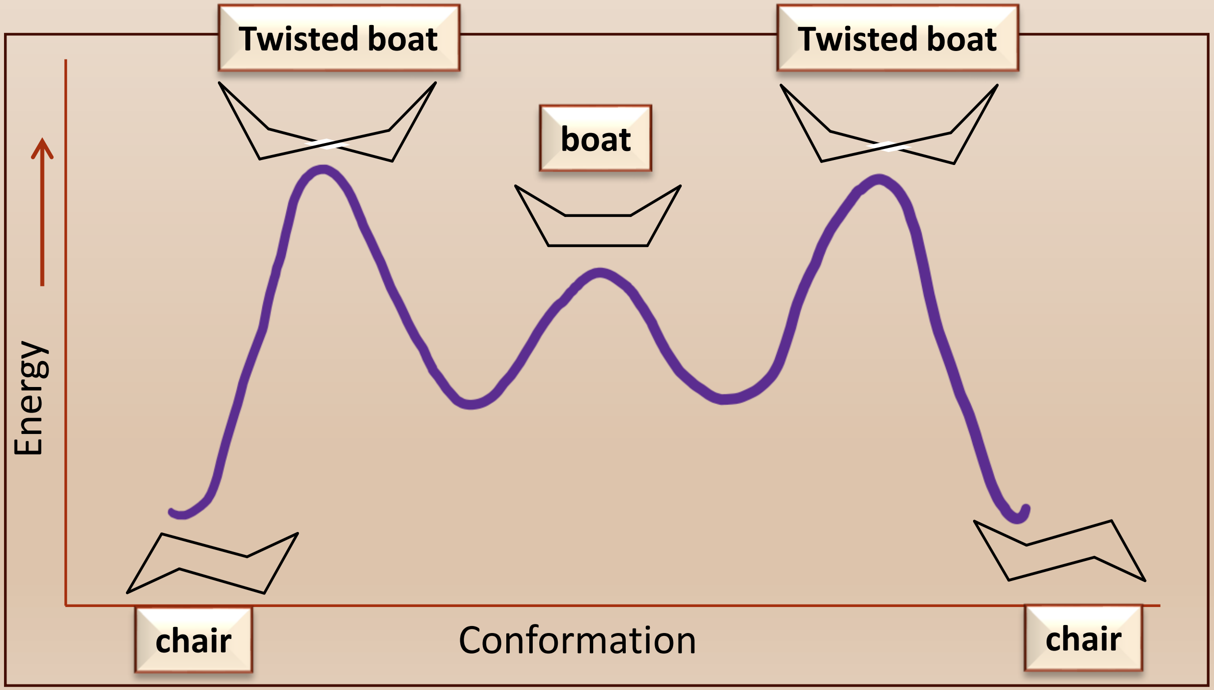

chair

The two chair conformations are lowest in energy which the twisted boat is highest in energy. Boat conformations fall in the middle. We will study only the two chair conformations of cyclohexane. You might think that they are identical, but in a 3D environment they are not as you will see in the later slides.

Conformation of Cyclohexane

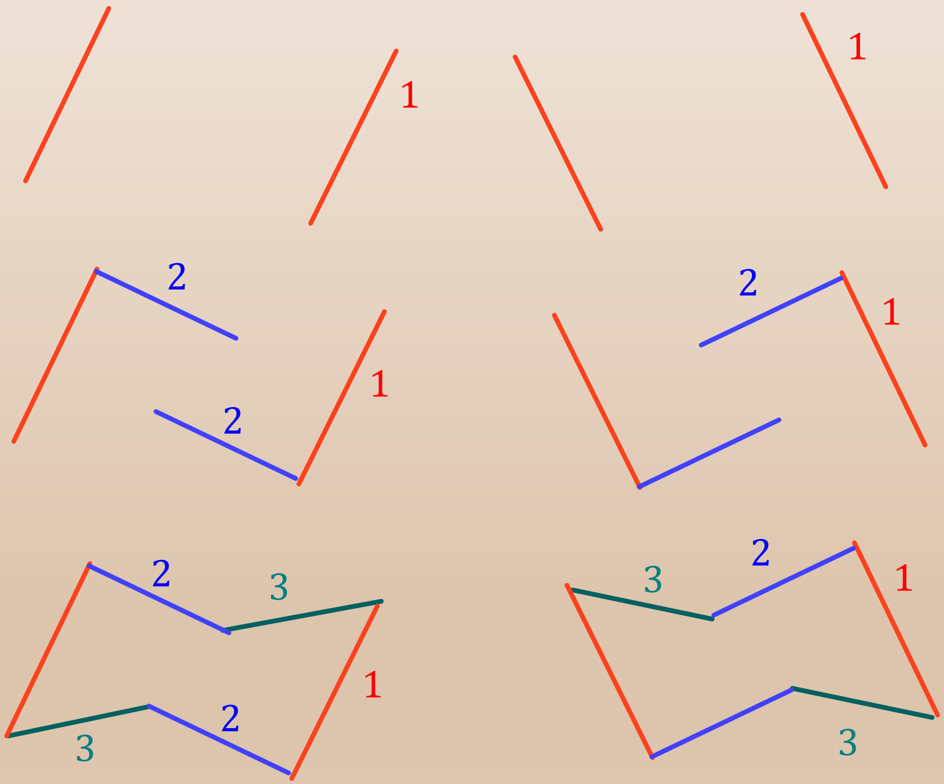
Below is the energy diagram for the cyclohexane ring flips. The most stable , low energy conformations are the chair conformations. The twisted boat and boat conformations are higher in energy and thus not stable enough to study.

- The two low energy chair conformations, formed by flipping from to the other, are the most studied conformers for cylcohexane.



How to Draw Cyclohexane

Follow the steps below to draw a professional looking ring structure. All the bond lengths should be the same. The ring flip drawing is the second column.



Step 1 Draw two parallel lines (shown in red), slanted downward and slightly offset from each other. These are first four carbons.

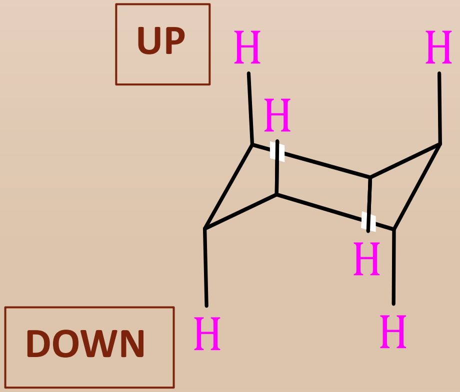
Step 2 Draw the next two lines (blue) parallel to eachother on opposite sides. These are the remaining two carbons.

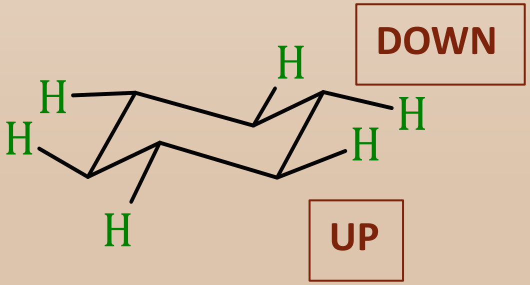
Step 3 Join the red and blue lines with two more parallel lines to form the final two bonds.

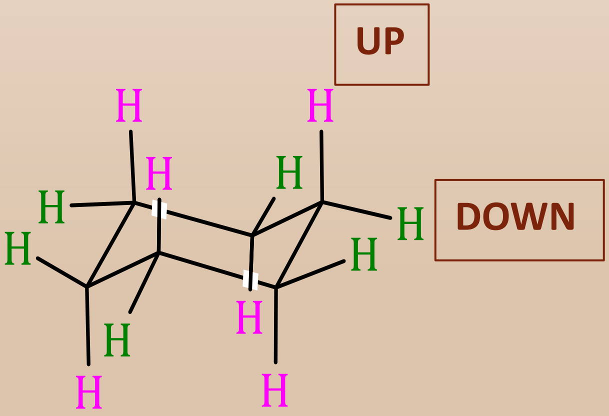
Drawing the Axial and Equatorial Hydrogens

The twelve hydrogens in a cyclohexane ring have two different orientations: 6 are axial (**a**), going up and down while 6 are equatorial (**e**), also going up and down. The first two structures show just these two orientations, pink for axial and green for equatorial. The third structure shows all the hydrogens together.

Observe that one axial H is going up, the next one is going down – 180^o dihedral angle. The same is true for equatorials – but the dihedral angle is 60^o here. In the third structure see that when the axial H is going up, the equatorial H is going down.





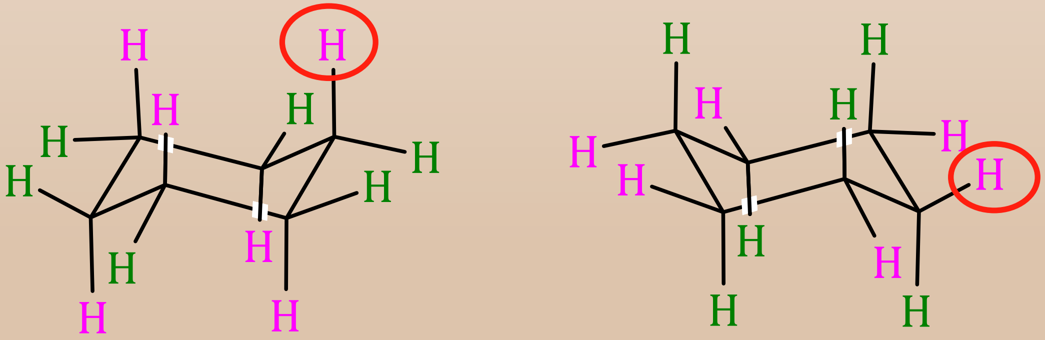


Conformation (ring flip) of Cyclohexane

When one chair conformation flips to the other , the second chair conformation has the hydrogens flipped from axial to equatorials. This interconverting, resulting in the exchange of axial and equatorial positions by a ring-flip occurs for all groups, whether hydrogen or any other group on that carbon.

Note that the axial H going up in the flipped chair is the now the equatorial H still going up.

- See a YouTube video here to see the ring flip: **LINK**
- See another one here….**LINK**

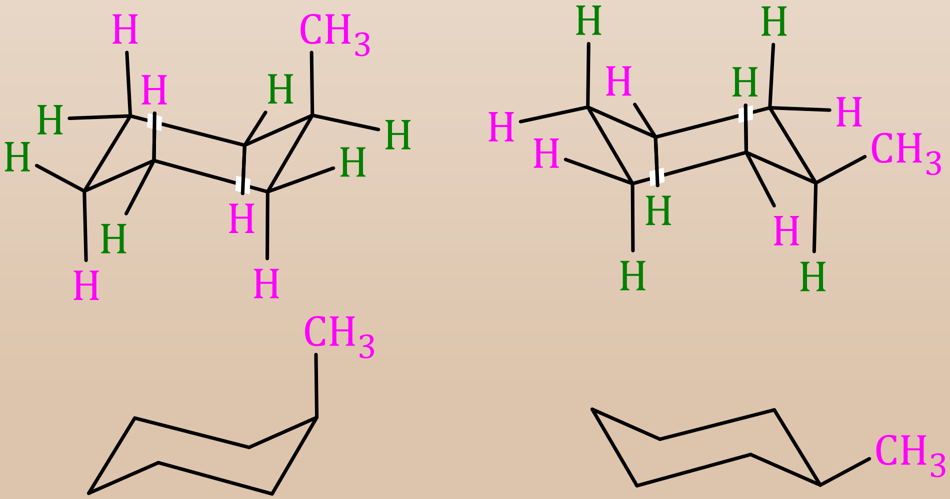


Watch the video (Conf Video 6) to understand a and e H in cyclohexane ring flip. See link in the "Description".

Conformations of Methyl Cyclohexane

Methylcylcohexane will have one methyl group substituted on the carbon. Below are two flip structures. The axial methyl group becomes equatorial, both going up. The structures below are without all the hydrogens. It is better to draw without the hydrogens.

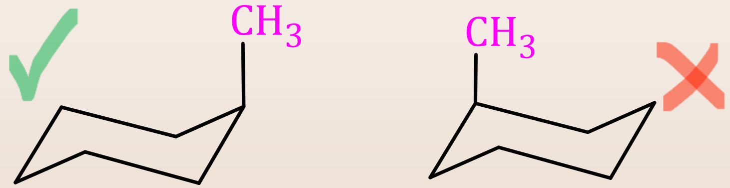
The cyclohexane with methyl group in the equatorial position is more stable (lower in energy) because there is less steric hinderance from other groups.



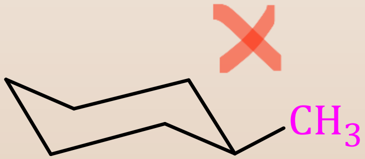
Watch the video (Conf Video 7) for this molecule. See the link in the "Description".

Some General Rules for Writing Conformers

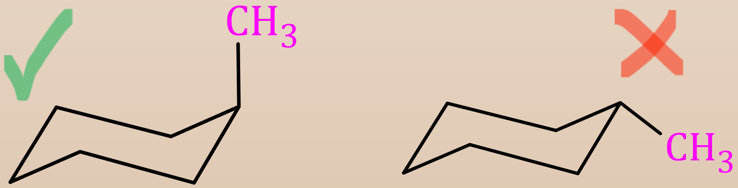
- Always start writing your substituents in the chair conformation on the top right carbon.



- Write the first chair conformer as I have shown on the right. It is easier to draw.



- Start with that group being axial.



In general, big groups are more stable in equatorial positions due to less steric tension/hinderance.

Conformation of Disubstituted Cyclohexane

Disubstituted cyclohexanes can have distinct conformers with low and high stability (energy) depending on where the two groups are, axial or equatorial. The cis and trans geometry also will help to decide how the two groups interact with each other.

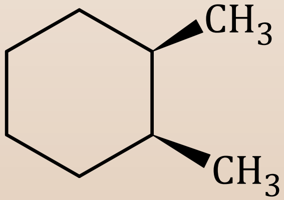
There are 6 isomers of dimethylcylcohexane.

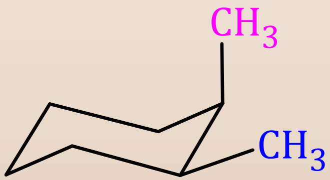
(cis)-1,2-dimethylcyclohexane	(trans)-1,2-dimethylcyclohexane
(cis)-1,3-dimethylcyclohexane	(trans)-1,3-dimethylcyclohexane
(cis)-1,4-dimethylcyclohexane	(trans)-1,4-dimethylcyclohexane

The next few slides show how these structures look in the chair conformation and which conformer is more stable (lower in energy).

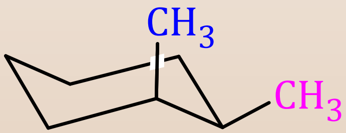
1,2-dimethylcyclohexane

- *Cis*-1,2-dimethylcylohexane will have one methyl group in axial and one in equatorial position. This conformation is where the two groups are going in the same direction. I have drawn the "up" conformation, but they can be down also. When the ring flips, the pink axial goes to equatorial position.





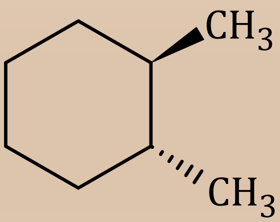
a, e

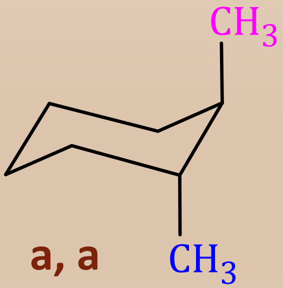


a, e

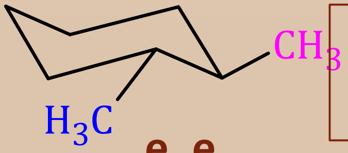
Both are equal in energy and stability.

- *Trans*-1,2-dimethylcyclohexane will have both methyl groups in axial position because they are going in opposite direction. When the ring flips, both become equatorial.





a, a



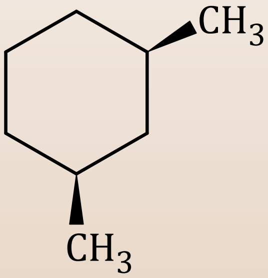
e, e

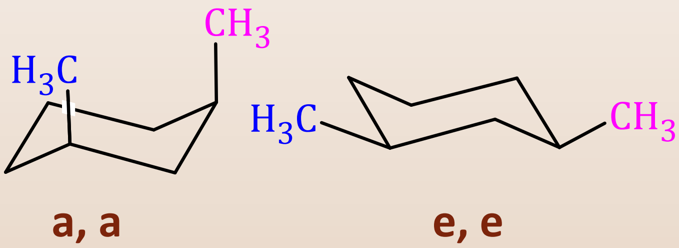
e,e conformer is lower in energy.

Watch the video (Conf Video 8) showing these structures. See the link in the "Description".

1,3-dimethylcyclohexane

- *Cis*-1,3-dimethylcylohexane prefers a cis-diequatorial conformation



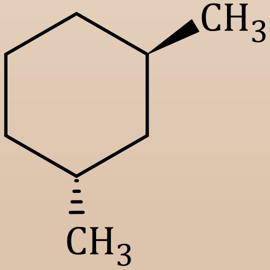


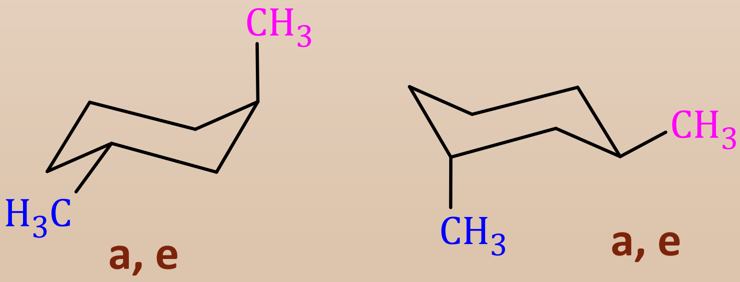
a, a

e, e

The e,e is more stable with lower energy.

- *Trans*-1,3-dimethylcyclohexane exists in an axial-equatorial conformation (the only ones possible).





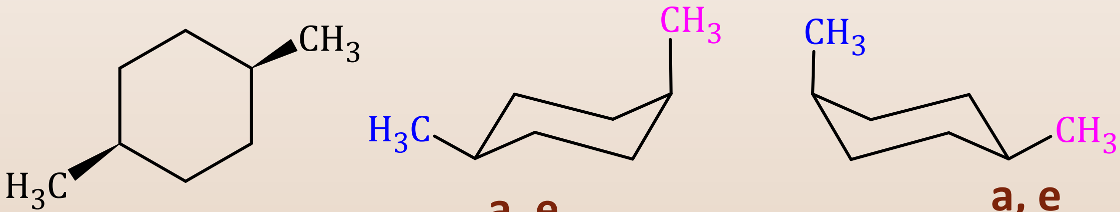
a, e

a, e

Both are equal in energy and stability.

1,4-dimethylcyclohexane

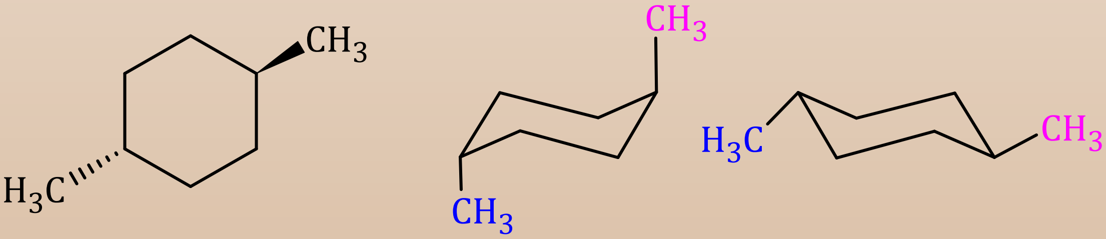
- *Cis*-1,4-dimethylcylohexane prefers a *trans*-diequatorial conformation



a, e **a, e**

Both are equal in energy and stability.

- *Trans*-1,4-dimethylcyclohexane exists in an axial-equatorial conformation (the only ones possible)

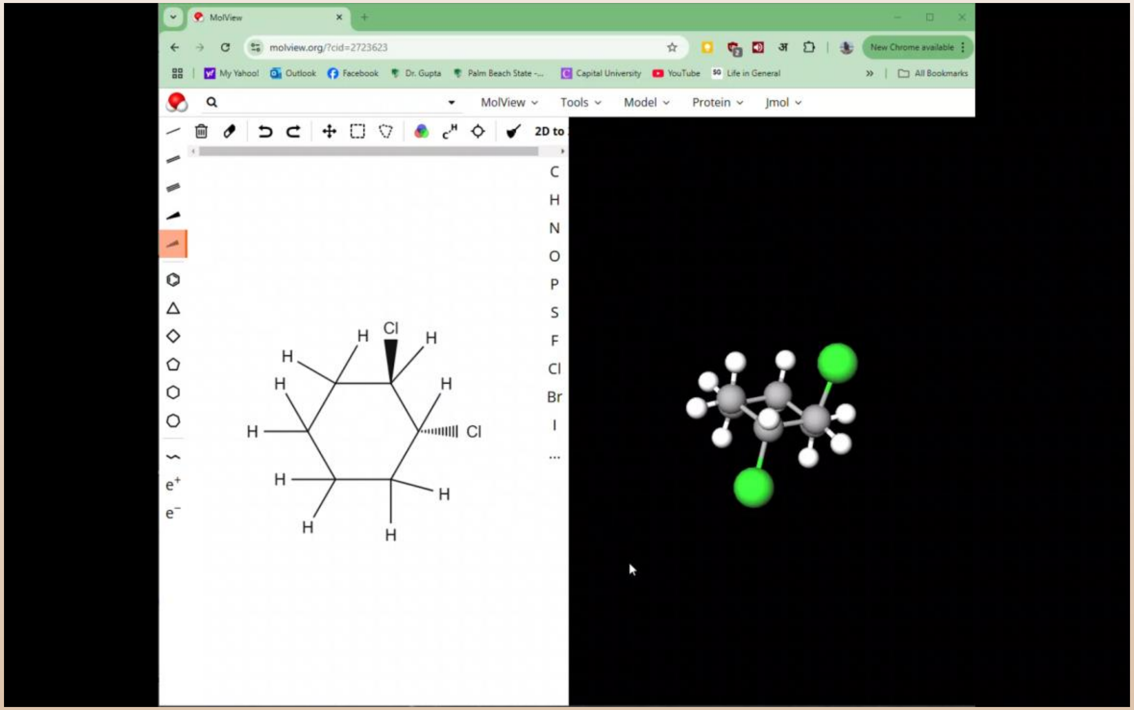


a, a **e, e**

The e,e is more stable with lower energy.

Cis and Trans relationship

Here is the video for trans 1,2-dimethylcyclohexane using MolView. (https://molview.org/)



Key Words/Concepts

- Conformation
- Anti
- Gauche/staggered
- Eclipsed
- Torsional strain
- Angle strain
- Steric strain (steric hindrance)
- Cis and trans isomers (geometric isomers)
- Chair conformation
- Equatorial and axial substituents