Conformational Analysis

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These are all the same compound - all the atoms are attached in the same way. However, they are in different conformations, which arise from rotating various bonds.

Conformation Vs Configuration

Free rotation about C-C single bond produces conformation Energy difference between 0.8 kCal/mol to 6 kCal/mol Conformer/rotamer cannot be seperated Conformation is only rotation without breaking bond Eg. Ethane, nbutane,cyclopentane, cyclohexane

Configuration is due to C=C Or C=C, arrangment or asymetric C-atom Energy difference is 100K Cal/mol or more Isomer can be separated by energy In configuration old bonds break and new bonds formed. Eq. Maleic Acid, Fumeric acid, 1,2-dichloroethene

Rotation or bond breaking???

And now for a different configuration altogether ...

Conformation and cc

Some conformations are more





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Newman projections are subject to a few conventions

- The carbon atom nearer the viewer is at the junction of the front three bonds
- The carbon further away (which can't in fact be seen in the end-on view) is represented by a large
- circle. This makes the perspective inaccurate—but this doesn't matter
- Bonds attached to this further carbon join the edge of the circle and do not meet in the centre
- Eclipsed bonds are drawn slightly displaced for clarity—as though the bond were rotated by a tiny

fraction









Are rings planner?

- Lets assume a fully saturated carbocyclic rings
- Each carbon is sp3 hybridized
- Then each bond angle would ideally be 109.5°.
- However, in a planar ring, the carbon atoms don't have the luxury of choosing their bond angles: internal angle depends only on the number of atoms in the ring.
- If this angle differs from the ideal 109.5°, there will be some sort of strain in the molecule.





all internal angles 109.5°

The Trend

The ring strain is largest for threemembered rings but rapidly decreases through a four-membered ring and reaches a minimum for a five-membered ring

A planar five-membered ring is predicted to have the minimum level of ring strain

The ring strain keeps on increasing (although less rapidly) as the rings get larger after the minimum at 5

Number of atoms in ring 3	Internal angle in planar ring 60°	109.5 °- internal angle ^a 49.5°
4	90°	19.5°
5	108°	1.5°
6	120°	-10.5°
7	128.5°	-19°
8	135°	-25.5°
^a A measure	of strain per carl	bon atom.



The Trend

Heats of combustion for some straight-chain alkanes

Straight-chain alkane	CH ₃ (CH ₂) _n CH ₃ : n =	- $\Delta H_{ m combustion}$, kJ mol ⁻¹	Difference, kJ mol ⁻¹
ethane	0	1560	
propane	1	2220	660
butane	2	2877	657
pentane	3	3536	659
hexane	4	4194	658
heptane	5	4853	659
octane	6	5511	658
nonane	7	6171	660
decane	8	6829	658
undecane	9	7487	658
dodecane	10	8148	661





Stable



Smaller Ring systems





http://research.cm.utexas.edu/nbauld/teach/cycloprop.html







Baeyer Strain



Adolf von Baeyer

(1835 – 1917)

In 1885, Adolf von Baeyer a German chemist proposed Baeyer's strain theory to explain the relative stability of cycloalkanes.



- $\frac{1}{2}$ [normal angle reduced angle] 1 [(2n-4) [(2n-4)]
- $\frac{1}{2}\left[109^{\circ}28' \left[\left(\frac{2n-4}{n}\right)90^{\circ}\right]\right]$
- n= number of C-atom in a cycle.
- Eg. Cyclopentane
- $\frac{1}{2} \left[109^{\circ}28' \left[\left(\frac{2(5)-4}{5} \right) 90^{\circ} \right] \right]$
- $\frac{1}{2} \left[109^{\circ}28' \left[\left(\frac{10-4}{5} \right) 90^{\circ} \right] \right]$ • $\frac{1}{2} \left[109^{\circ}28' - \left[\left(\frac{6}{5} \right) 90^{\circ} \right] \right]$

- $\frac{1}{2}$ [109°28′ 108°]
- $\frac{1}{2}[1^{\circ}28'] \bullet (1^{\circ} = 60')$
 - $\frac{1}{2}[60'+28']$
- $\frac{1}{2}[88']$
- [0°44′]
 - Baeyer Strain in cyclopentane

Advantages

- Cyclopropane, cyclobutane have higher angle strain. Hence, they are more reactive.
- Angle strain in cyclopentane is minimum. Hence, it is most stable.
 - The relative stabilities of cycloalkanes up to cyclopentane can be explained satisfactorily.

Limitations

- According to the theory, cyclohexane is less stable than cyclopentane. However, cyclohexane and other higher cycloalkanes are found to be more stable than cyclopentane.
- The theory gives planar model of cycloalkanes.
- Carbon-carbon double bond is easily formed. But according to Baeyer's strain theory it is difficult to form.









If you were to join six tetrahedral carbon atoms together, you would probably find that you ended up with a shape like this.



the carbon skeleton for cyclohexane



cyclohexane as a "chair"









direction shown

...gives a slightly different conformation in which the eclipsing interactions have been reduced: the "twist-boat:" conformation an end-on view of the twist-boat conformation shows how the eclipsing interactions have been reduced

Guidelines for drawing cyclohexane these hydrogen atoms are all 'up' relative to their partners on the same C carbon these hydrogens are all 'down' relative to their partners on the same C atom

The carbon skeleton

Trying to draw the chair conformation of cyclohexane in one continuous line can lead to some dreadful diagrams. The easiest way to draw a chair conformation is by starting off with one end.

Next draw in two parallel lines of equal length.

At this stage, the top of the new line should be level with the top of the original pair.

Finally, the last two lines should be added. These lines should be parallel to first parallel lines

and the lowest points should also be level.

LEVEL



these lines should be parallel

these lines should be parallel

Adding the hydrogen atoms

This is often the trickiest part. Just remember that you are trying to make each of the carbon atoms look tetrahedral. (Note that we don't normally use wedged and hashed bonds; otherwise things get really messy.)

The axial bonds are relatively easy to draw in. They should all be vertically aligned and alternate up and down all round the ring.

The equatorial bonds require a little more care to draw. The thing to remember is that each equatorial bond must be parallel to two C–C bonds.

> put in all 6 equatorial C-H bonds

notice the 'W' shape here, . .

... and the 'M' shape here

in each diagram, all the red bonds are parallel



Common mistakes

If you follow all the guidelines above, you will soon be drawing good conformational diagrams. However, a few

how not to draw cyclohexanes ...



common mistakes have been included to show you what not to do!

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the chair has been drawn with the middle bonds horizantal, so the upper points of the chair are not level. This means the axial hydrogens can no longer be drawn vertical the axial hydrogens have been drawn alternating up and down on the wrong carbons. This structure is impossible because none of the carbons can be tetrahedral the red hydrogens have been drawn at the wrong angles – look for the parallel lines and the 'W' and 'M'

The ring inversion (flipping) of cyclohexane



ring inversion of a monosubstituted cyclohexane notice that the hydrogen atom shown changes from axial to equatorial













Disubstituted Cyclohexanes

 i. Substituents prefer equatorial rather than axial positions in order to minimize the steric strain created of 1,3-diaxial interactions.
 ii. The more stable conformation will place the larger substituent in the equatorial position.









Cis and trans stereoisomers of 1,3dimethylcyclohexane

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CH₃

Summary of Disubstituted Cyclohexane Chair Conformations

AA/EE

Both axial substitution creates strong 1,3 – di axial interaction

Both Equatorial substitution creating No 1,3 – diaxial interaction

AE/EA

One substituent on axial One substituent on equatorial

Equal 1,3- di axial interaction in both conformers if same type substituent If different substituent – Larger sub will favor equatorial position

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