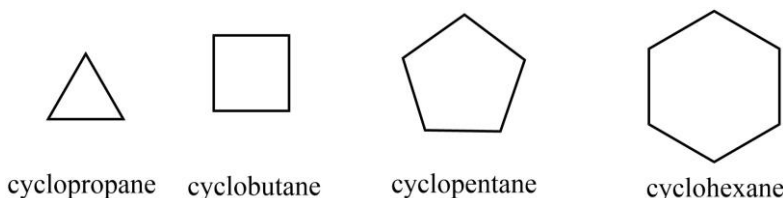


❖ Conformational Analysis of Cycloalkanes (Upto Six Membered Rings)

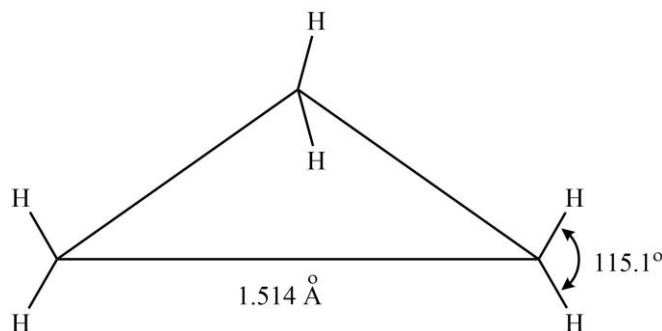
Most of the cyclic compounds can be categorized on the basis of the number of atoms participating in the cyclic skeleton and their special properties. Rings with 3 or 4 atoms are quite rigid and extremely strained because of their large deviation from the normal tetrahedral angle ($109^{\circ}28'$) which gives rise to a very high angle strain and the presence of a very large magnitude of torsional strain as well.



Most common rings have 5–7 members and can be characterized by the normal tetrahedral angles and groups oriented outward from the cycle. Rings with 8–11 members are labeled as medium rings and can be characterized by transannular interactions which is a strain produced by groups pointing inward from the cycle. Furthermore, if the number of atoms is equals to or greater than 12 (large rings), very low strain exists and such rings are pretty much comparable with the corresponding acyclic hydrocarbons. In this section, we will discuss the conformational analysis of cycloalkanes up to six-membered rings.

➤ Conformations of Cyclopropane

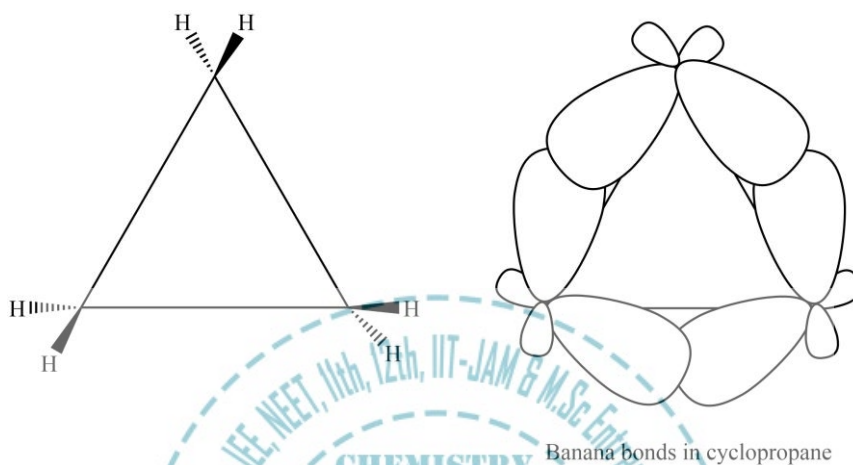
Cyclopropane is a kind of cycloalkanes with C_3H_6 as the molecular formula and is consisted of three carbon atoms that are connected with each other to give a cyclic structure. Each carbon atom is also bound with two hydrogens symmetrically so that the point group becomes D_{3h} . There is a huge ring strain in the cyclopropane due to its smaller size.



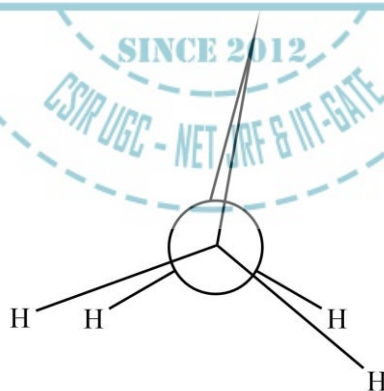
cyclopropane

The trigonal structure of cyclopropane needs the carbon-carbon bond angles to be at 60° ; however, it is much smaller than the ideal bond angle of 109.5° (most stable thermodynamically and is generated for bonds with sp^3 hybridized orbitals) and gives rise to the large magnitude of ring strain.

The cyclopropane molecule also possesses a very high torsional strain arising from the eclipsed conformation of its H atoms. Per se, the bonds between the C atoms are significantly weaker than in an archetypal alkane, giving rise to much higher reactivity in this case. Also, the nature of bonding between the carbon atoms is usually described in terms of bent or banana bonds, where the carbon-carbon bonds are bent outwards so that the inter-orbital angle becomes equal to 104° .



All this decreases the magnitude of bond strain and is obtained by distorting the sp^3 hybridized orbitals of carbon atoms to theoretically an sp^5 hybridized orbitals (i.e. $1/6$ contribution of s orbital and $5/6$ contribution of p orbital) so as to make C-C bonds have more π -character than usual (and giving s-character same time the carbon-to-hydrogen at the more bonds gain).

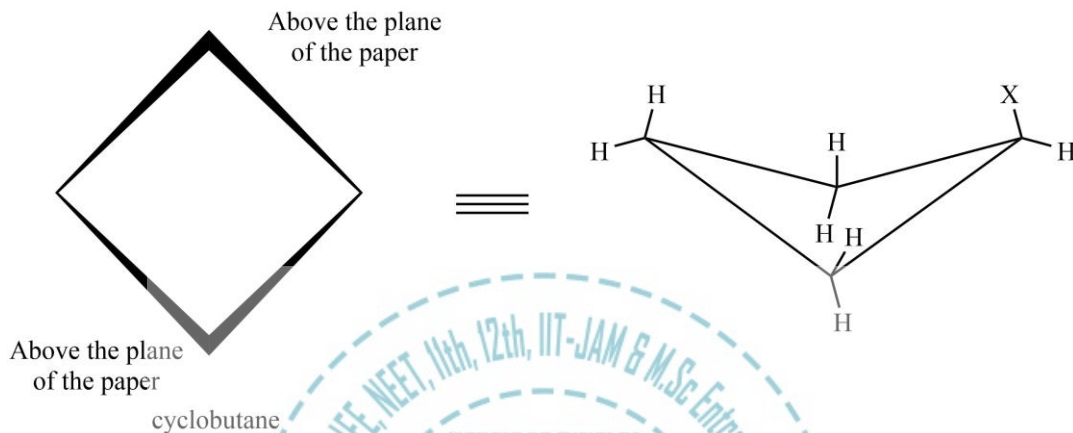


Newman projections of cyclopropane

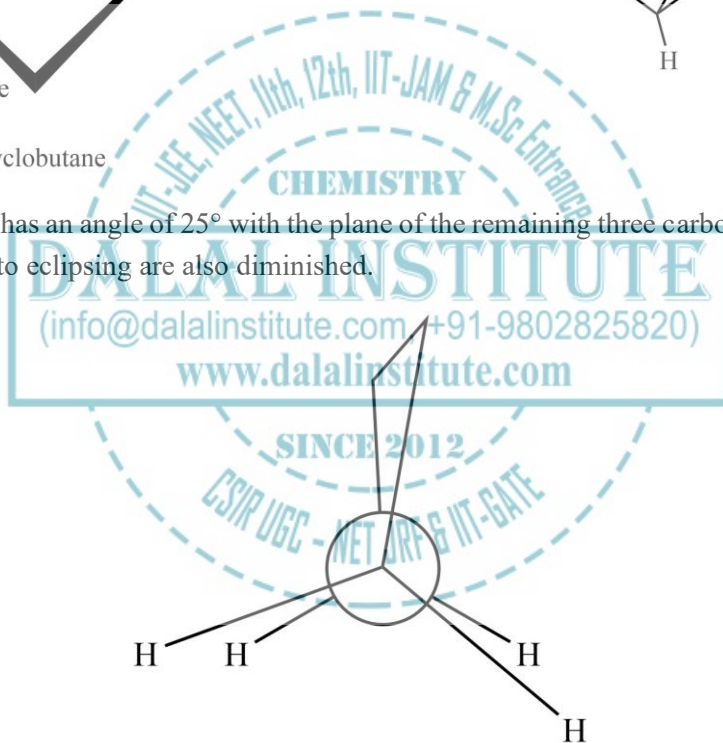
One uncommon consequence of bending of bonds is that while the C-C bonds in cyclopropane are weaker than usual, the C atoms are also closer together than in a normal alkane bond: 151 pm versus 153 pm, when the average alkene bond length is about 146 pm.

➤ **Conformations of Cyclobutane**

The angles between carbon-carbon bonds in cyclobutane are quite strained, and therefore, have lower bond dissociation energies than corresponding unstrained or linear hydrocarbons like cyclohexane or butane. Furthermore, the cyclobutane molecule is very unstable above 500 °C. As far as the structure is concerned, four carbons in cyclobutane are not in a single plane but adopts a puckered or somewhat "folded" conformation.



Any single carbon also has an angle of 25° with the plane of the remaining three carbon atoms. Like this, some of the interactions due to eclipsing are also diminished.

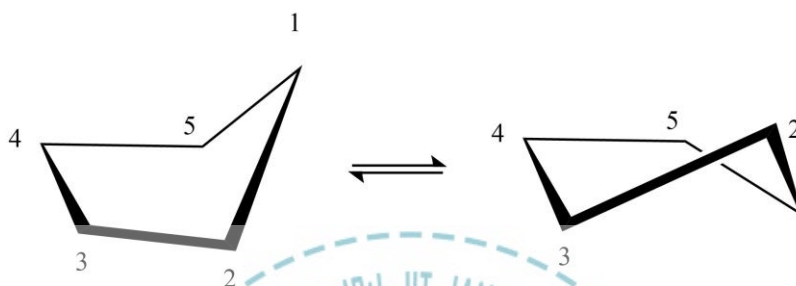


Newman projections of cyclobutane

The conformation of cyclobutane is also known as the "butterfly" structure. Furthermore, it is also worthy to note that equivalent puckered conformations of cyclobutane interconvert within each other at room temperature due to an appropriate supply of thermal energy.

➤ **Conformations of Cyclopentane**

The cyclopentane is the second-most common cycloalkane (after cyclohexanes) and stabler than cyclobutanes. Its planar conformation has almost zero angle strain but a huge magnitude of torsional strain resulting in a non-planar conformation, which in turn, actually increases angle strain slightly but still favorable due to stability from reduced torsional strain. The cyclopentane undergoes a rapid bond rotation process At room temperature where every carbon has its turns of being at the endo site eventually.



Conformational equilibrium of cyclopentane

The 'envelope' conformation (left) of cyclopentane is of the lowest energy where the out-of-plane carbon (i.e., 1 in the left side structure) is said to be in the 'endo or inside' site. The enveloping eliminates the torsional strain along the sides and the envelope's flapping happens. Nevertheless, the neighboring C atoms are eclipsed at the envelope's plane and are situated away from the fold.



Newman projections of cyclopentane

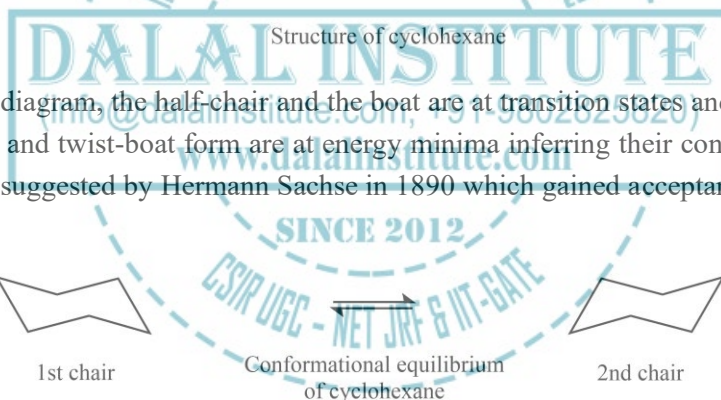
Furthermore, if we view Newman's projection of cyclopentane molecule signed down one of the carbon-carbon bonds reveals the staggering nature of carbon-hydrogen bonds.

➤ Conformations of Cyclohexane

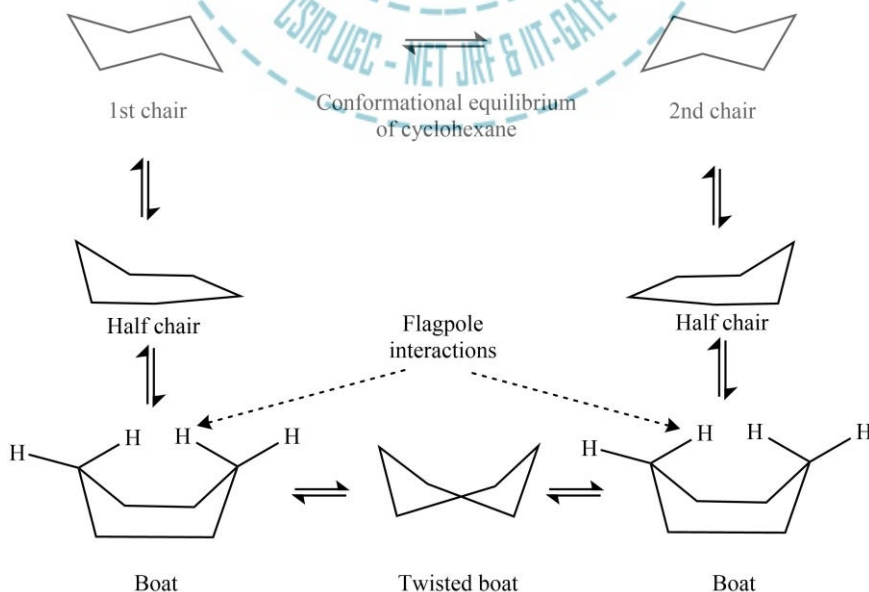
Many students confuse the polygon formula of cyclohexane molecule with its actual structure and assume that it must be planar. Nevertheless, its structure is far from a perfect hexagon because the conformation of a flat 2-dimensional planar hexagon would have a huge magnitude of angle strain. After all, its carbon-carbon bonds would not be at the ideal tetrahedral angle (i.e., 109.5°). Furthermore, the torsional strain would also be of significant magnitude in hexagonal structure because all of the bonds would be of eclipsed type. So, to decrease torsional strain, the cyclohexane adopts a 3-dimensional geometry (chair form), which interconvert at room temperature very rapidly via the chair flipping mechanism during which 3 other intermediate conformations are met: the first one is the half-chair (most unstable), a more stable boat conformation, and the third one is the twist-boat (more stable than the boat but less stable than the chair form).



Structure of cyclohexane



In the potential energy diagram, the half-chair and the boat are at transition states and signify energy maxima whereas the chair form and twist-boat form are at energy minima inferring their conformer nature. The chair conformation was first suggested by Hermann Sachse in 1890 which gained acceptance at a widespread level in the later period.



In the chair form, the carbon-carbon bond angles become 109.5° , and therefore, the angle strain was completely eliminated. Also, six out of twelve hydrogens were parallel to the principal axis (C_3 -axis), and are called axial hydrogens; whereas the remaining hydrogens are at higher angles from the principal axis imparting the label of equatorial hydrogens.

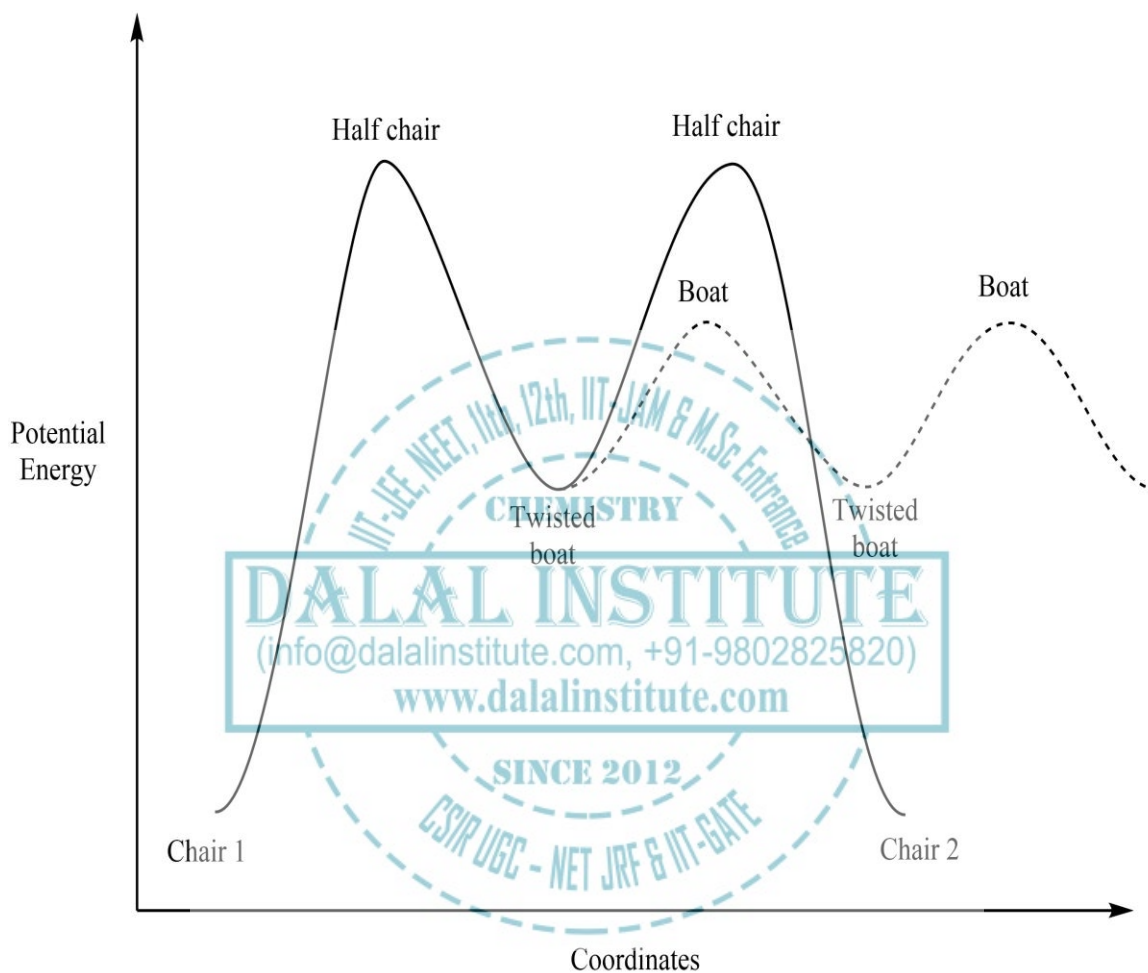


Figure 1. Potential energy diagram for different conformations of cyclohexane molecule.

Another important confirmation of cyclohexane molecule is known as the boat form which also gets interconverted to the more stable chair form. Furthermore, if the mono-substitution occurs at cyclohexane, it will most likely happen at the equatorial site because of the less torsional strain. Finally, the cyclohexane molecule has the lowest magnitude of torsional and angle strain of all cycloalkanes available making the cyclohexane a strain-free system.

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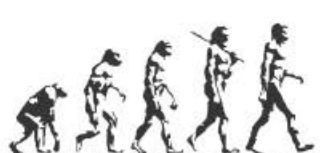
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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