Conformations

A carbon–carbon single bond is formed when an sp^3 orbital of one carbon overlaps with an sp^3 orbital of a second carbon. Because σ-bonds are cylindrically symmetrical, rotation about a carbon–carbon single bond is possible without any change in the amount of orbital overlap.

The different spatial arrangements of the atoms of a molecule that result from rotation about a single bond are called conformations. A specific conformation is called a conformational isomer or a rotamer.

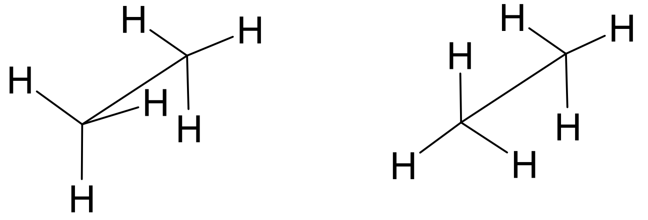
Conformations of Ethane

When rotation occurs about the carbon–carbon bond of ethane, two extreme conformations can result:

- Staggered conformation
- Eclipsed conformation

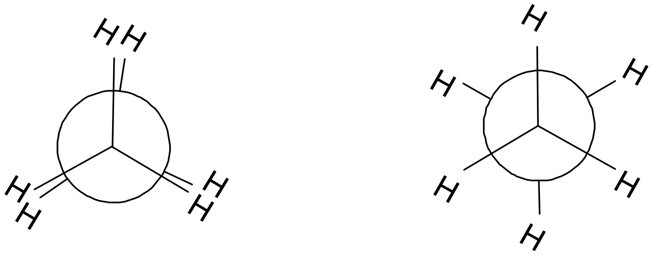
An infinite number of conformations are possible between these two extremes.

The two conformations can be represented by:



Eclipsed Staggered

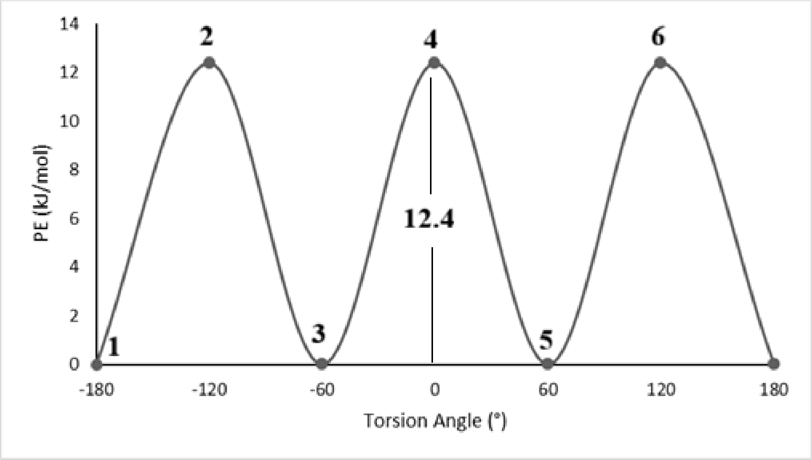
Sawhorse projection

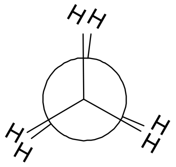


Newman projection

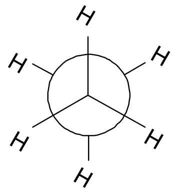
Stability of Ethane Conformations

The staggered conformation of ethane is more stable than the eclipsed conformation. The destabilisation associated with the eclipsed form is due to torsional strain. It is generated by the slight repulsion of electron pairs of adjacent C–H bonds. The energy difference between the two conformers (or the barrier of interconversion between the two conformers) is about: 12.4 kJ mol^{-1}.





2,4,6



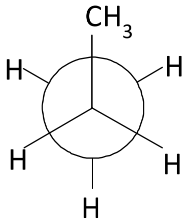
1,2,3

Conformation of Propane

Like ethane, propane also has two important conformers:

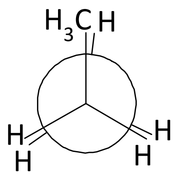
- Eclipsed form
- Staggered form

The energy barrier between the eclipsed and staggered forms is:14.2 kJ/mo. This barrier is slightly higher than that of ethane. The energy barrier is largely contributed by torsional strain. Steric interaction due to the methyl group has insignificant role here**.**



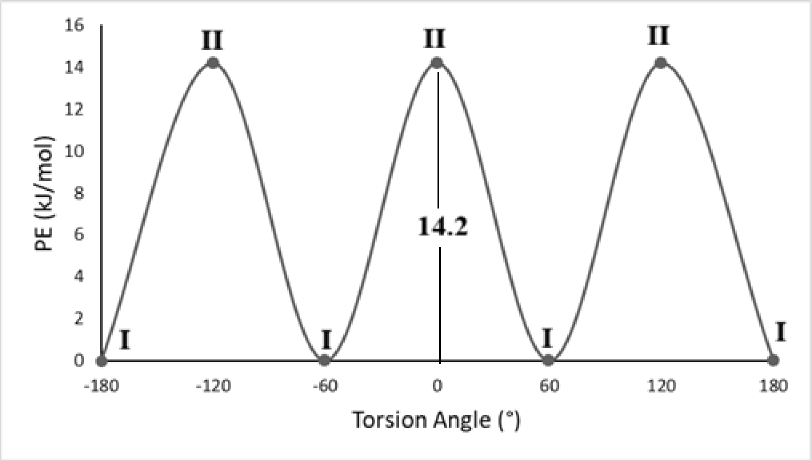
I

Staggered



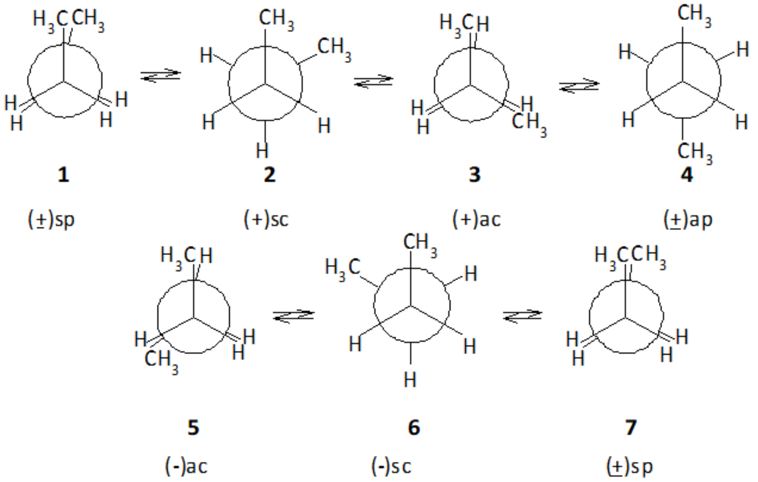
II

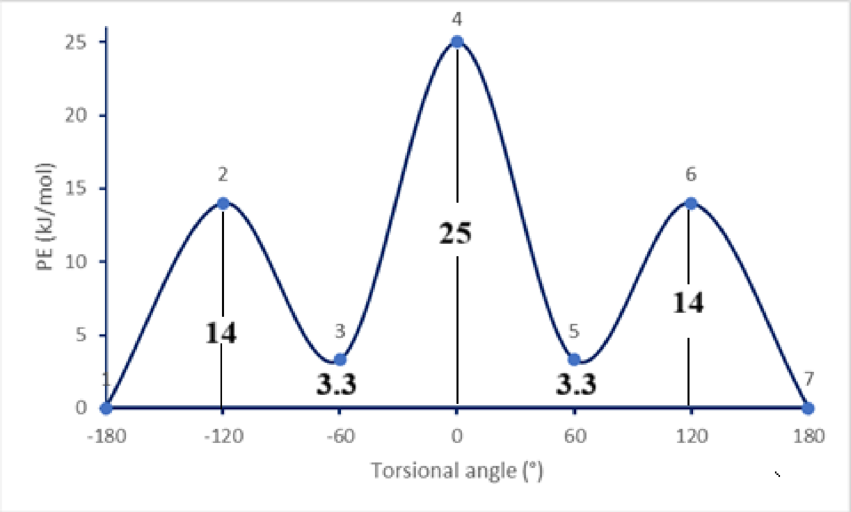
Eclipsed



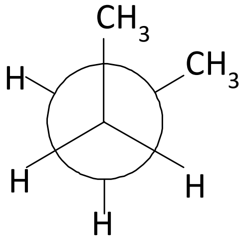
Conformation of n-butane

In n-butane there are three energy barriers to rotation about C2—C3 bond and three energy minimum energy conformations are distinguishable. The Newman projections for the energy barriers and energy minimum are drawn below:

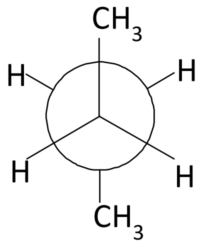




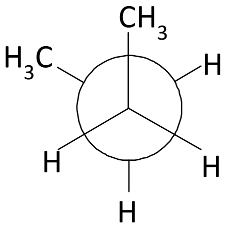
Energy minimum conformations



P-gauche



anti



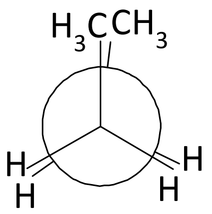
M-gauche

The two gauche forms (P-gauche and M-gauche) are non-superposable mirror images of each other and form an enantiomeric pair. They are equienergetic and have a potential energy of 3.3 kJ/mol above that of the anti-form. This amount of energy (3.3 kJ/mol) comes from the steric interaction of the two methyl groups at a torsion angle of 60°, by comparison with the anti-position. This interaction is named butane-gauche interaction. The gauche interaction originates from the non-bonded interaction between the two gauche methyl groups whose distance falls within the van der Walls group radii.

The anti-form is the most stable. Here the torsional strain is absent and the H—H and CH_3—H skew interactions are very small. It has a centre of symmetry, a C_2 axis and a σ-plane.

Energy barriers

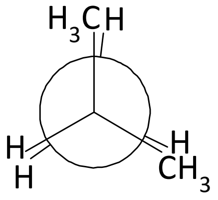
Synperiplanar or fully eclipsed is the maximum energy conformation. The higher energy barrier (25 kJ/mol) arises from van der Waals net repulsive interactions, principally between the eclipsed methyl groups, and torsional strain owing to the eclipsing of three pairs of vicinal bonds.



Synperiplanar

or

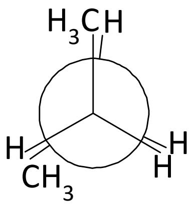
Fully eclipsed



anticlinal

or

partially eclipsed



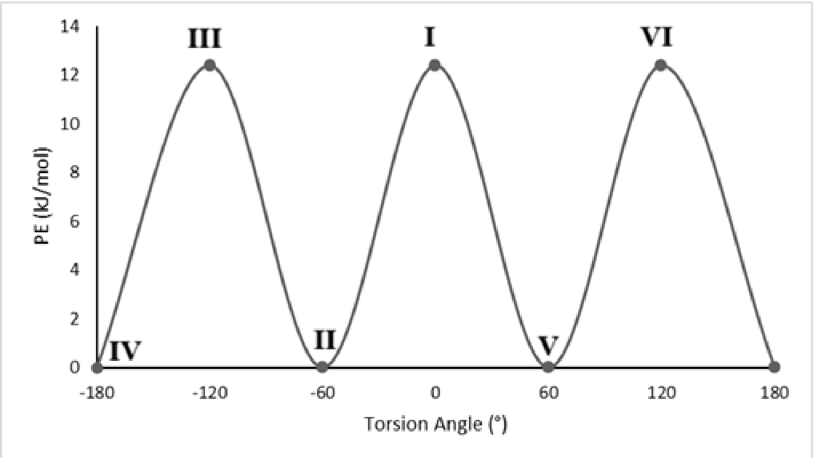
anticlinal

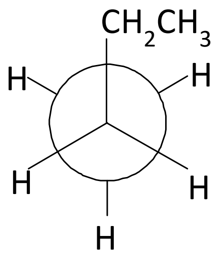
or

partially eclipsed

The two anticlinal forms are partially eclipsed conformations. Torsional strains originated from the three eclipsing pairs are likely to be the reason behind this energy barrier (14 kJ/mol). Van der waals repulsion between H and CH_3 is considered to be very insignificant here.

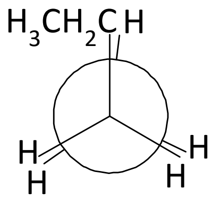
<u>Conformational energy curve of n-butane about C1—C2 bond rotation</u>





II,IV,V

Staggered



I,III,VI

Eclipsed

Population of conformers:

At 25°C, there is only one molecule of eclipsed ethane for each 160 of staggered ethane. Thus, the population of eclipsed ethane is negligible. At room temperature (25°C), n-butane contains 66% of the anti-form, 17% of P-gauche, and 17% of M-gauche, the last two forming a racemic mixture. As the T increases, the population of the less stable conformer increases and eventually becomes equal to that of the stable conformer. On the other hand, at low temperature, the most stable anti conformer prevails to a much greater extent and may become the only form detectable.

Baeyer Strain Theory (1885)

German chemist Adolf von Baeyer proposed in 1885 that cycloalkanes are planar rings and that their stability depends on angle strain. According to him, instability in a cycloalkane arises due to the deviation of the C–C–C bond angle from the normal tetrahedral angle (109°28′ ≈ 109.5°). The greater the deviation from 109.5°, the greater the angle strain, and hence the lower the stability.

Deviation from Tetrahedral Angle and Predicted Stability

Ring	Internal Angle of Planar Polygon	Deviation from 109.5°	Predicted Angle Strain	Predicted Stability (Baeyer)
Cyclopropane	60°	49.5°	Very high	Least stable
Cyclobutane	90°	19.5°	High	More stable than cyclopropane
Cyclopentane	108°	1.5°	Very small	Highly stable
Cyclohexane	120°	10.5°	Moderate	Less stable than cyclopentane

Stability Trend According to Baeyer's Theory:

Cyclopentane > Cyclohexane > Cyclobutane > Cyclopropane

Failure of Baeyer's Strain Theory

The theory assumes that all rings are planar, which is true only for 3- and 4-membered rings (approximately planar). Bayer's theory predicts that cyclopentane is the most stable ring. However, experimental data (heat of combustion per –CH_2– group) shows that cyclohexane is actually the most stable ring. Therefore, Baeyer's assumption of planar rings had to be abandoned.

Origin of strain in rings:

The overall strain in a cyclic molecule in the absence of electronic effects and secondary linkages originates from three factors:

(i) Bayer strain or angle strain: Bayer strain is a consequence of deforming bond angles from their optimal tetrahedral value of about 109°25'.

(ii) Pitzer strain (or torsional strain): Pitzer strain or torsional strain originates from the eclipsing of adjacent bonds. It is not basically steric in nature and is best explained in terms of electron-electron repulsion between the occupied covalent bonds.

(iii) Non-bonded interactions: When the two non-bonded atoms or groups are separated by a distance equal to the sum of their van der Waals radii, their mutual attractive interaction is maximum. When this distance separating two atoms or groups is less than sum of their van der Waals radii, repulsive force dominates over attractive force. Such non-bonded interactions are also known by different names such as steric hindrance and van der Waals interactions, steric strain, etc.

Conformations of cyclohexane:

Two forms of cyclohexane have been proposed:

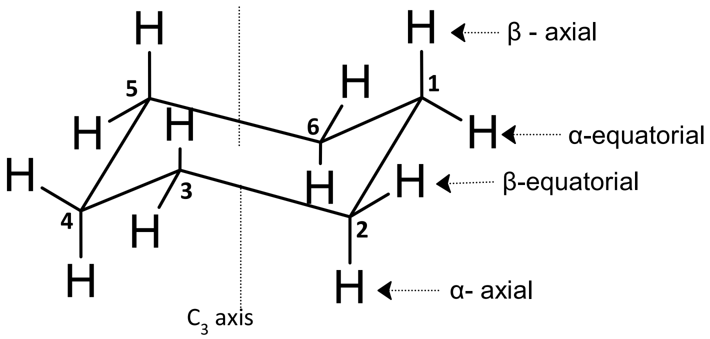
(i) chair form
(ii) boat form.

According to many experimental studies, the stable form of cyclohexane is the chair form.

(i) Chair conformation

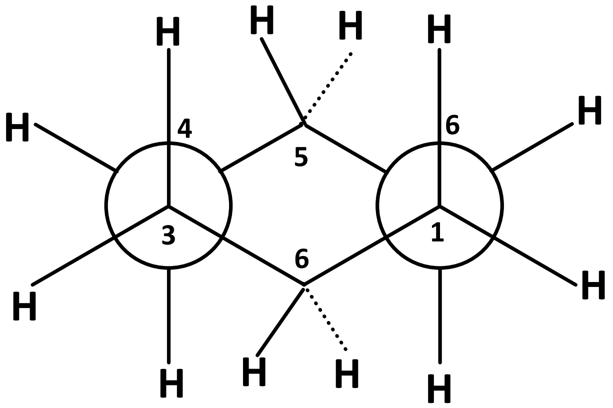
1. Geometry: The electron diffraction experiments of cyclohexane in the gaseous phase show the following geometrical parameters:

- C–C bond length = 152.8 pm
- C–H bond length = 111.5 pm
- C–C–C bond angle = 111.05' (instead of 109.28')
- Dihedral angle = 58° (instead of 60°)



Sawhorse projection of chair conformation

The increased C–C–C bond angle makes the chair conformation slightly flattened so that the dihedral angles between C–C bonds are 58° and vertical C–H bonds (axial) are not exactly parallel to the C_3 axis but lean outwards from it by 7°. The flattening brings a balance between angle strain and torsional strains, thus minimizing the energy of the system.



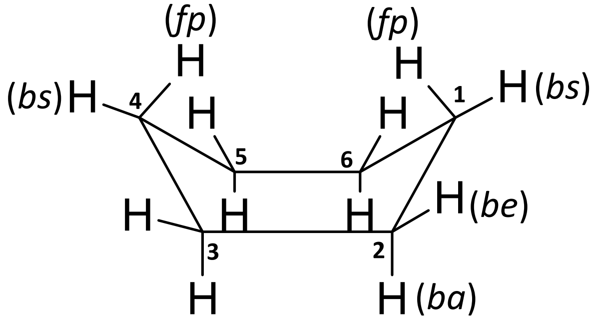
Newman projection of chair conformation

The Newman projection shows the staggered arrangement of bonds.

2. Symmetry: It has a three-fold proper axis of symmetry (C_3 axis) along with three C_2 axes perpendicular to C_3 axis. It also has an S_6 axis. There are three σ_d planes. Chair conformation also has a centre of inversion. This belongs to symmetry point group D_{3d}.

(ii) Boat conformation

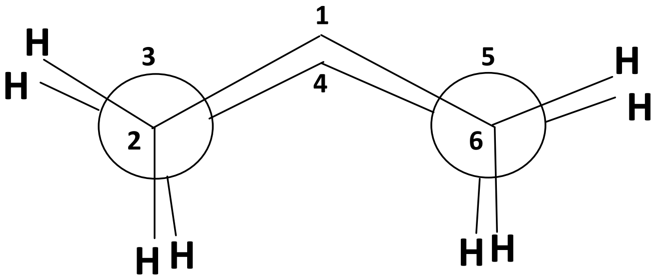
Another conformation of cyclohexane, which is free from angle strain is boat form.



In boat conformation, there are four types of C–H bonds designated as:

- Flagpole (fp)
- Bowsprit (bs)
- Boat-equatorial (be)
- Boat-axial (ba)

It has a C_2 axis and two planes of symmetry (σ_v). It belongs to point group C_{2v}.



Newman projection for boat conformation

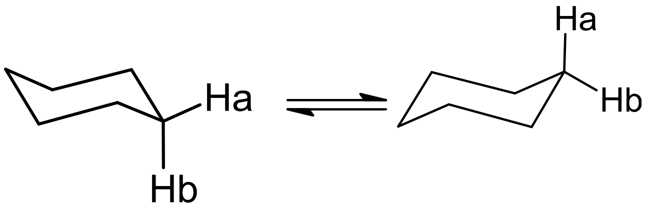
The Newman projection reveals the eclipsed interactions present in the boat form.

Comparison of stability of chair and boat forms:

Chair form has six butane-gauche interactions arising out of a set of four consecutive carbon atoms: 1-2-3-4, 2-3-4-5, 3-4-5-6, 4-5-6-1, 5-6-1-2, 6-1-2-3. Boat form has four butane-gauche interactions (1-2-5-6, 3-4-5-6, 2-3-4-5, 2-3-1-6). However, the boat form has four pairs of eclipsed C–H interactions while eclipsed interactions are absent in chair form. There also exists a very strong steric repulsion between the flagpole hydrogens at C-1 and C-4. As a result of these eclipsed C–H interactions and flagpole C–H interactions, total strain in boat conformation is significantly higher than in chair conformation. Consequently, the boat form is less stable than chair form by an amount of energy around 26-28.9 kJ/mol.

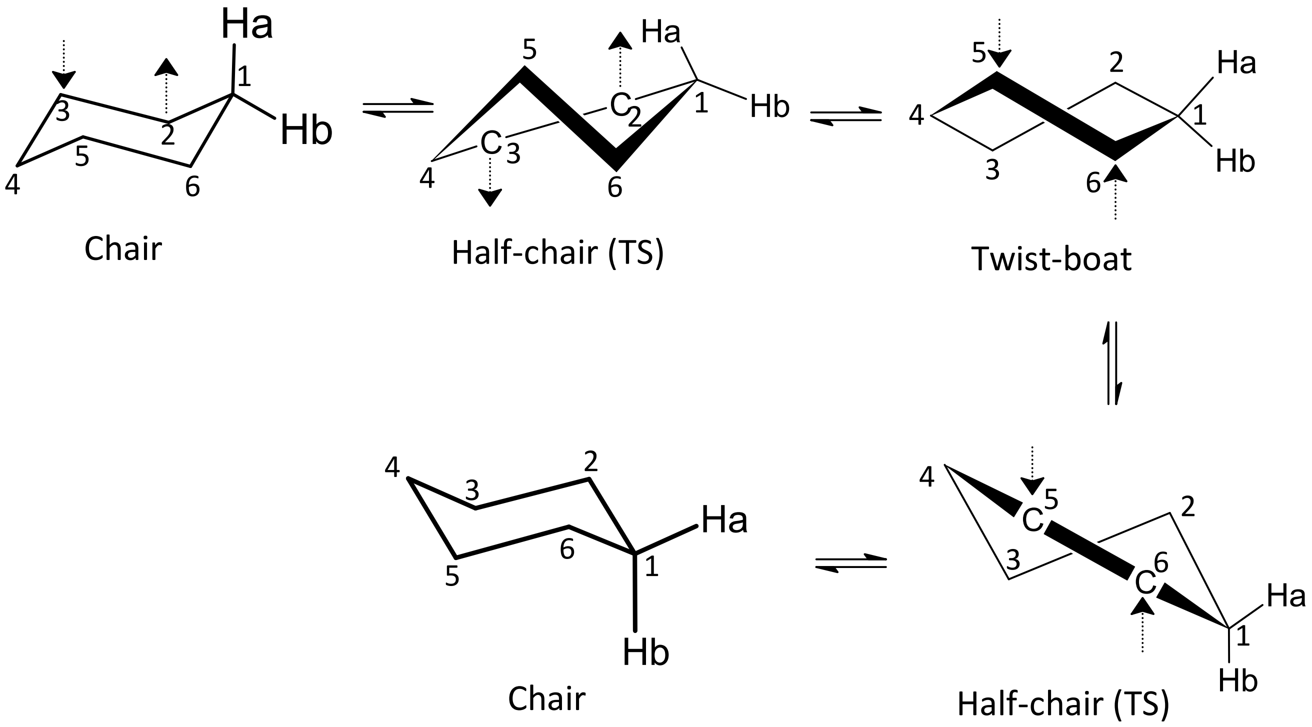
Conformational inversion of chair form of cyclohexane

Cyclohexane undergoes a ring inversion or a ring flipping at ambient temperature. During inversion one chair form flips into an equivalent chair form, axial hydrogens become equatorial and vice versa.

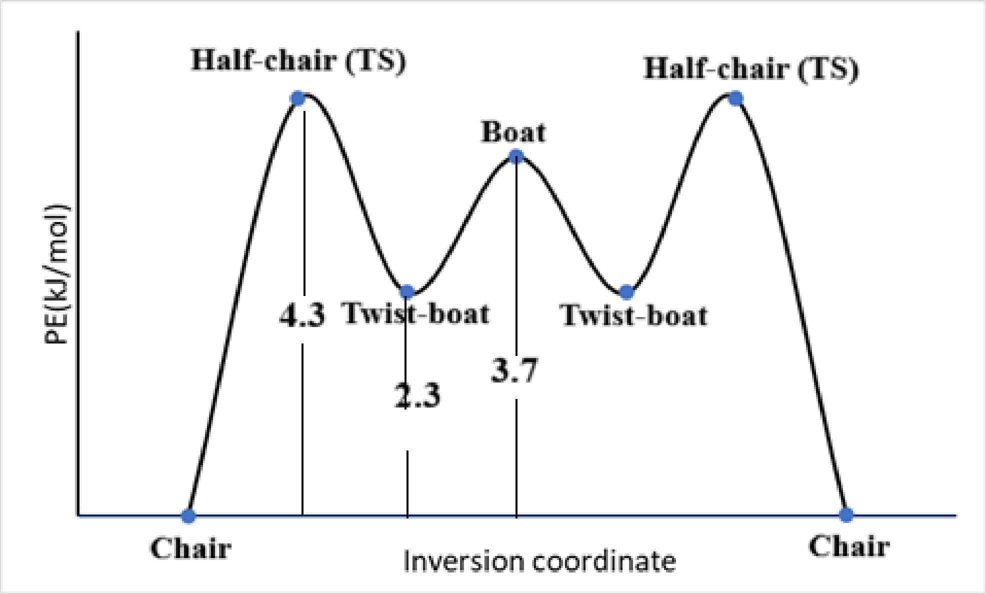


Mechanism

The whole inversion process can be broken down into the conformations shown below:

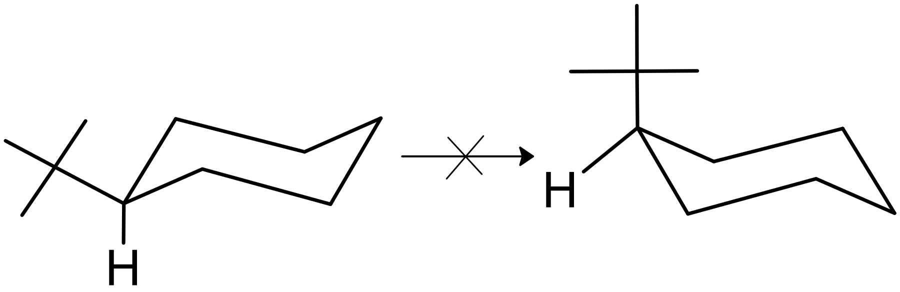


The energy profile for this ring inversion process shows that the half-chair conformation is the energy maximum on going from a chair to twist-boat. The true boat conformation is the energy maximum on interchanging between two mirror image twist boat conformers.



Freezing of Conformational Inversion

Cyclohexane normally undergoes rapid chair–chair interconversion (ring inversion) at room temperature. However, this conformational mobility can be “frozen” by introducing a bulky substituent into the ring. Bulky groups such as the tert-butyl group, $(CH_3)_3C$–, strongly prefer the equatorial position. If such a large group were forced into the axial position, severe steric interactions (especially 1,3-diaxial interactions) would occur, causing significant ring strain and a large increase in energy. As a result, in tert-butyl substituted cyclohexane, the chair conformation in which the tert-butyl group occupies the equatorial position becomes overwhelmingly more stable. The alternative chair form, where the group would be axial, is so energetically unfavorable that ring inversion is effectively prevented at ordinary temperature.



Questions

1. What are conformers or conformational isomers? Draw sawhorse projections and the corresponding Newman projections for the important conformations of ethane. Draw energy profile diagram for the conformations with respect to rotation around the C—C bond. Which one is more stable conformation of ethane and why?
2. Draw the Newman projections for all the conformers of n-butane that result from rotation about C2—C3 bond. Show the potential energy change against angle of rotation.
3. Draw Newman projections for all the energy minimum conformers of n-butane. Label them as anti, P-gauche and M-gauche. Compare their stability with explanations.
4. Discuss the Bayer strain theory. Mention its failures.
5. Draw Sawhorse and Newman projections of the chair and boat forms of cyclohexane. Compare their stability. Draw energy profile diagram for the different conformers of cyclohexane.