Stereoisomers

Stereoisomers are isomers which have the same molecular formula and same structure but differ in the arrangement of atoms or groups in space. Stereoisomers can be classified into the following two types:

Configurational Isomers **Conformational Isomers**

Configurational Isomers

Configurational Isomers like conformational isomers arise due to the difference in the spatial arrangement of atoms or groups in a molecule. However, the energy difference between configurational isomers is large and hence one isomeric form cannot be easily converted into the other isomeric form.

Configurational Isomers can be classified into two types:

Optical Isomers Geometrical Isomers

Conformational Isomers

Conformational Isomers are isomers that show different spatial arrangement around a single bond, for example, the ethane molecule is known to exist in a large number of different forms of spatial arrangement. The highest and lowest energy arrangements are known as the eclipsed and the staggered conformational forms. Newman and Sawhorse were the two scientists, who suggested methods for the diagrammatic representation of the different conformational forms. These methods helped in representing the three dimensional molecules in a simple manner.

Newman’s Projection Formula

Newman’s Projection Formula involves the viewing of the molecule end-on, that is along the bond joining the two carbon atoms. The two carbon atoms joined by the bond are represented as two superimposed circles; however for representation only one circle is drawn. The centre of the circle represents the front carbon atom C1 whilst the circumference represents the second carbon atom C2. The line joining the two carbon atoms is not visible. Bonds attached to the C1 carbon atom i.e. the front carbon atom, are drawn as straight lines from the center and the bonds attached to C2, the second carbon atom are drawn as straight lines from the circumference of the circle. The projected angle between each bond is kept as 120°.

The two forms of the ethane molecule, with the help of Newman’s Projection Formula, can be drawn as below in Fig. 1.

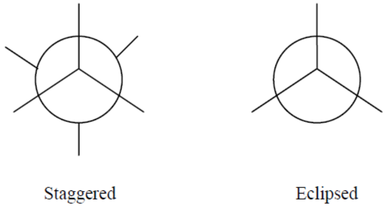


Fig.1. Ethane

The eclipsed form can be converted into the staggered form and vice versa by rotating the bonds attached to one of the carbon atoms by a 60^{o} angle. The bonds attached to the second carbon atoms are kept stationary.

In the staggered form, all the bonds attached to the C1 and C2 carbon atoms are maximum apart from each other whereas in the eclipsed form, the bonds attached to the two carbon atoms are closest to each other.

Energetically, out of the two forms, the staggered form is the more favored form. In the staggered form, all the bonds are maximally apart from each other, and it therefore has the least amount of stearic strain due to vander Waal repulsion. It also has the minimum repulsion between bond electrons. On the other hand, the bonds are closest to each other in the eclipsed form and it has the highest energy. The strain existing in the eclipsed form is termed as torsional strain. The energy barrier between the two forms in the ethane molecule has been experimentally found to be about 3 kcal/mol. The energy profile for the different conformational forms of ethane can be given as in Fig. 2.

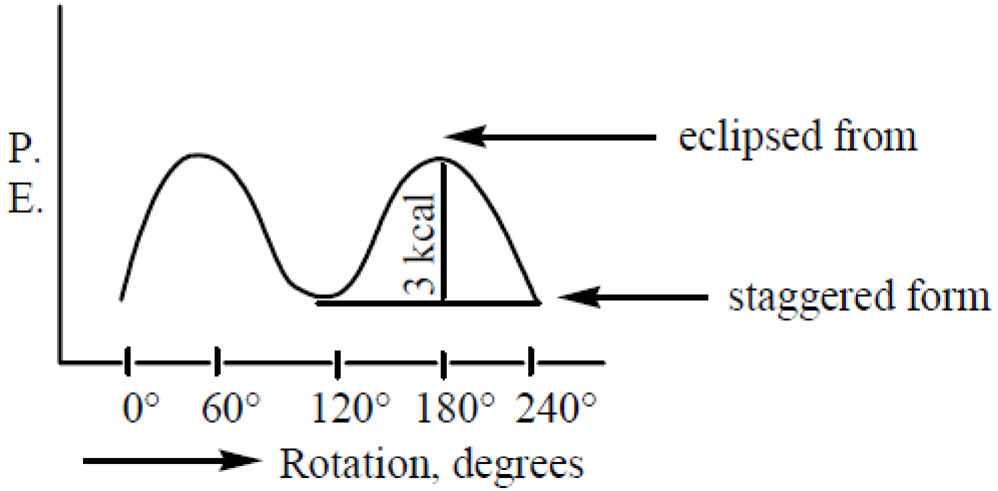


Fig. 2. Energy profile of ethane

Since the energy barrier between the staggered form and the eclipsed form in ethane molecule is very low, just 3 kcal/mol, the conversion of one form to the other form can occur readily. However, at any time most of the molecules of ethane exist in staggered form. The small energy barrier between them makes the isolation of the different conformational forms difficult. The conformational forms lying at the lower energy position in the energy profile graph are termed as conformers.

Conformations around any two adjacent carbon atoms in any molecule can be drawn in a similar manner. Different conformational forms available in a butane molecule, $CH_3CH_2CH_2CH_3$, around carbon atom 2 and 3 can be represented with the help of Newman Projection Formula as shown in Fig. 3.

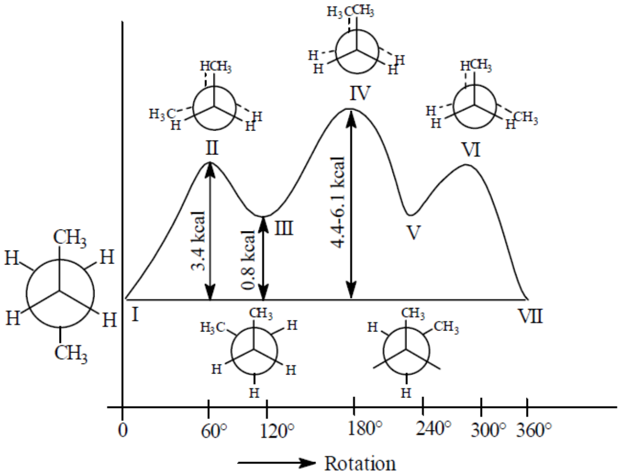


Fig. 3 Different Conformational Forms of n.butane around carbon atom 2 & 3

n-Butane shows the existence of two eclipsed conformational forms II and IV with different energies and two staggered conformational forms I and III having different energies. Staggered forms III and V are mirror image forms of each other and possess the same energy and are known as Gauche form. These are ~0.8 kcal higher in energy than the staggered form I. Eclipsed form II & VI possess the same energy. Stablest conformaton form is I with the lowest energy. Structure I and III are the more stable conformers.

However, in all the molecules, though the different conformational forms differ in their energy contents, the difference is so small that the energy available at ordinary temperature is enough for the conversion of the most stable form into the least stable form. Therefore, the different conformational forms are readily interconvertible and not isolatable.

Sawhorse Projection Formula

In Sawhorse Projection Formula a side view of the molecule is taken. The two carbon atoms are joined by a larger diagonal line which is taken to be on the plane of the paper. The remaining bonds are projected on paper by small lines drawn out from the terminal ends of the diagonal line. The heavy wedged bond projects the bond towards the viewer, the dashed bond projects the bond away form the viewer and the normal bonds lie in the plane of the page. The eclipsed and the staggered conformational form of the Ethane molecule can be represented with the help of Sawhorse Projection Formula as shown in Fig. 4.

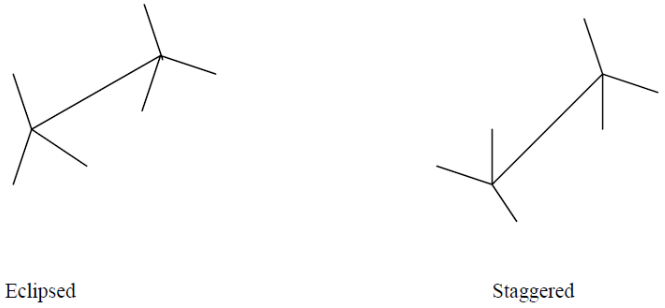


Fig.4. Conformations of Ethane

- **Conformational Isomers are also observed in alicyclic compounds for example in cyclohexane.**

The cyclohexane ring, if planar in nature would be unstable as the bond angle around each bond in the planar structure would be 120^{o}, a bond angle value of any hexagon structure. As the bond angle is 109. 28^{o} . for an sp^3 hybridized carbon atom, any deviation from this bond angle value in cyclohexane molecule would result in the instability of the molecule. However, cyclohexane molecule has been found to be stable. Heat of combustion values experimentally determined for cyclohexane molecule has been found to be 936.9 kcal/mol which is similar to the theoretically calculated value for a cyclohexane molecule. Theoretically the heat released, per methylene group, on combustion of any open chain hydrocarbon, to give CO2 and H2O is approximately 156.1 kcal/mol.; as cyclohexane shows the same value of the heat released on combustion, per methylene group, the molecule is as stable as any open chain compound.

The stability of the cyclohexane molecule can be explained on the basis that the ring, in order to acquire normal tetrahedral bond angle value, does not remain planar, but gets puckered.

The bonds pucker in a manner that each angle acquires a value of 109o28’, that of a normal sp3 hybridized carbon atom. Puckering results in giving the molecule four different conformational forms: the Chair, the Boat, the Twist and the Half boat form. The following Fig. 5 gives the energy profile of the different conformational forms of the cyclohexane ring.

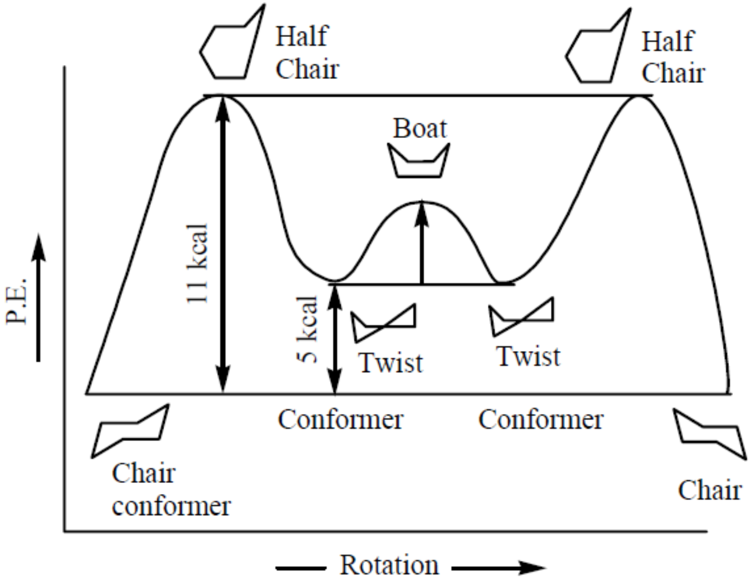
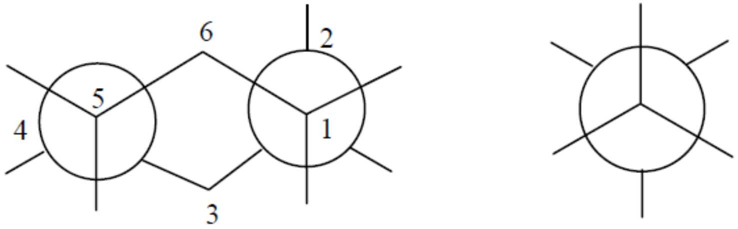


Fig. 5. Energy Graph of Conformations of Cyclohexane

- The energy diagram shows that the Chair and the twist forms lie at the energy minima and are the conformers.

- The chair form is the most stable form as the molecule is almost free of angle strain and has minimal amount of torsional strain. All the carbon atoms, adjacent to each other, in the chair form of the molecule are staggered with respect to each other.



Chair form of Cyclohexane

Staggered form of Ethane

Fig. 6

The chair form has two types of bonds:

The Axial Bonds **The Equitorial Bonds**

If the cyclohexane ring is pulled out and all the carbon atoms come to lie in a plane, the axial bonds would be bonds lying above and below the plane of the carbon ring. The axial bonds ‘a’ above the plane of the ring would be attached at alternate positions 1, 3 and 5 and below the plane of the ring at alternate positions 2, 4 and 6. The six remaining bonds lie in the plane of the ring and are called equatorial bonds ‘e’. The chair form can be flipped. On flipping, the axial bonds get converted into equatorial bonds and equatorial to axial.

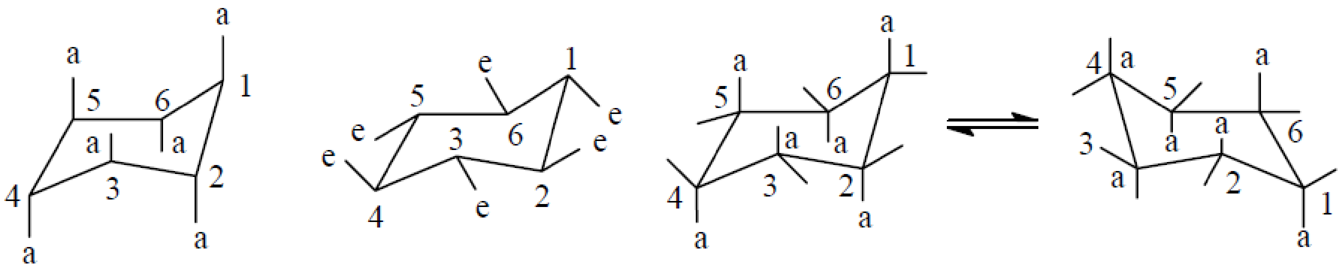


Fig. 7. Axial and Equitorial Bonds in the Chair form of Cyclohexane

The distance between any two axial bonds on the same side of the plane of the cyclohexane ring is 2.3 A^{o}, which is equal to the sum total of the vander Waals' radii of hydrogen atom, thus the cyclohexane ring is free of vander Waals' repulsion. However, if hydrogen at the axial position on the same side of the plane of the ring is replaced by any other group, then the molecule would become less stable, due to vander Waals' repulsion occurring between the group and the atoms existing on the other axial bonds. A substituent group present in cyclohexane is more stable in the equatorial position.

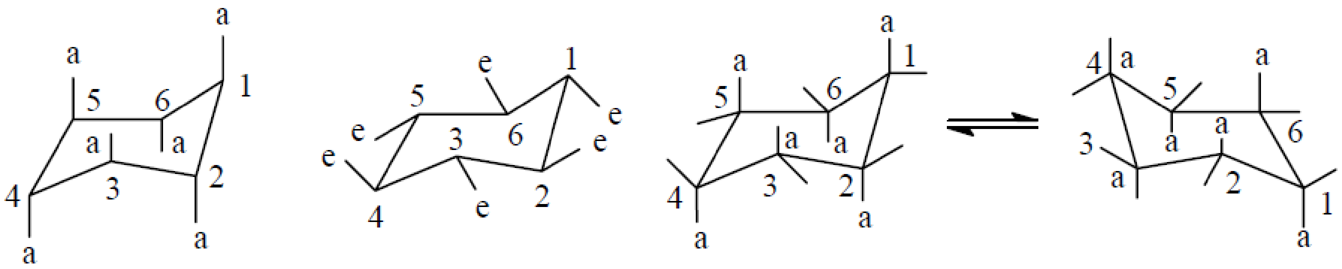


Fig. 7. Axial and Equitorial Bonds in the Chair form of Cyclohexane

- The boat form is energetically less stable because it has 2 pairs of adjacent carbon atoms 2, 3 and 5, 6 existing in the eclipsed conformational forms.

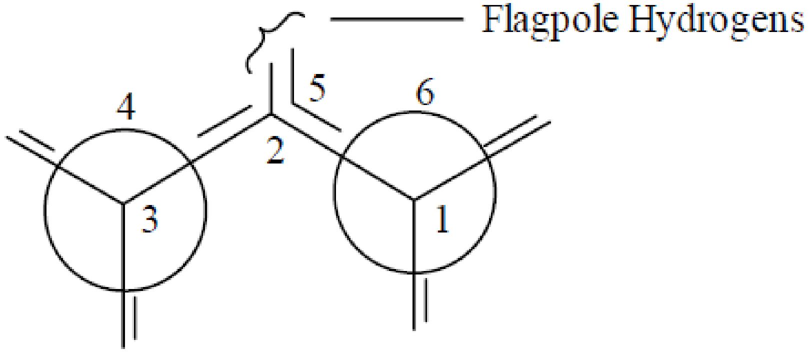


Fig 8. Boat form of Cyclohexane

Existence of the eclipsed conformational forms in the molecule, introduces torstional strain in the molecule and makes the molecule energetically less favourable. Also, the distance between the hydrogens attached to carbon atoms 2 and 5 is (1.80A^o) less than the sum total of the vander Waals radii of two hydrogen atoms i.e. 2.3A^o.

- Twist form, the molecule is energetically closer to the chair form. The twist form is more stable than the boat form as the flag pole hydrogens are still sufficiently apart.

- The half chair form is the least stable as the molecule partially acquires a planar structure and hence is subjected to a great amount of angle strain.

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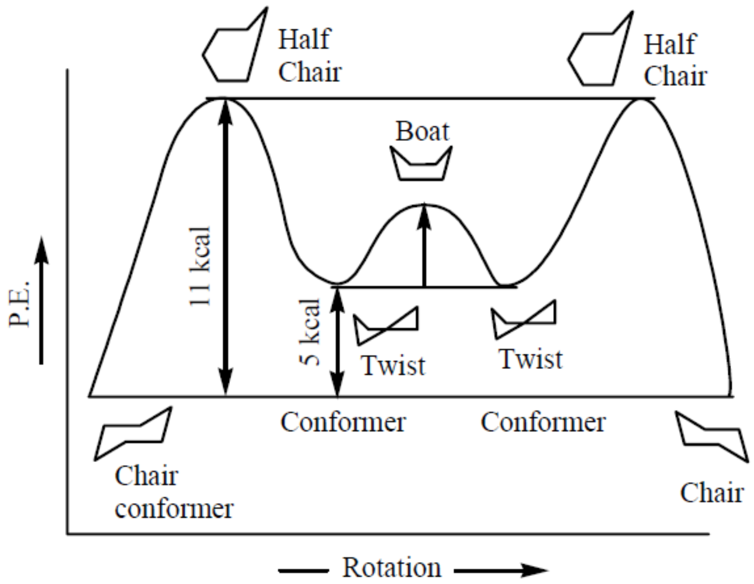

Fig. 5. Energy Graph of Conformations of Cyclohexane