Fig. 2.6.
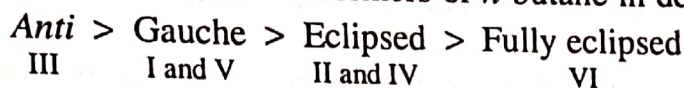
Thus, the relative stabilities of the six conformers of *n*-butane in decreasing order is as follows :

$$Anti > Gauche > Eclipsed > Fully\ eclipsed$$

       III   I and V   II and IV   VI

Molecule with carbon-carbon single bonds have many interconvertible conformers. Conformers cannot be separated because they rapidly interconvert.

2.27 CONFORMATIONS OF CYCLOALKANES

2.27.1 Stability of Cycloalkanes

Compounds with three and four membered rings are not as stable as compounds with five and six membered rings. The German chemist Baeyer (1885) was the first to suggest that the instability of these small ring compounds was due to **angle strain.** This theory is known as **Baeyer strain theory**.

Baeyer strain theory was based on the assumption that when an open-chain organic compound having the normal bond angle 109.5° (tetrahderal angle) is converted into a cyclic compound, there is deviation from the normal tetrahedral angle leading to the development of a strain in the molecule. This strain is called as angle strain or Baeyer strain. Baeyer assumed that rings are planar. Assuming that the rings are planar, the angle strain in various cycloalkanes can be expressed in terms of angle of deviation (distortion), *d*, *i.e.*, deviation from 109.5° for one bond.

$$d = \frac{1}{2}\left[109.5 - \frac{2(n-2)}{n} \times 90\right]$$
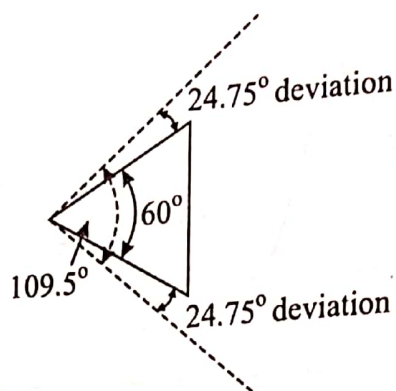
or

$$d = \frac{1}{2}(109.5 - \alpha)$$

where *n* = number of carbon atoms constituting the ring
        α = inner bond angle in the cycloalkane ring

$$\text{Angle strain} \propto d$$

$$\text{Stability} \propto \frac{1}{d}$$

The factor of $\frac{1}{2}$ is put in because the strain is spread over two bonds. For example, for cyclopropane ring the inner angle α is 60°, hence, $d = \frac{1}{2}(109.5 - 60) = 24.75°$. Similarly, the angle

strain can be calculated for rings of different sizes, e.g., $d = 9.75°$ for cyclobutane; 0.75° for cyclopentane; $-5.25°$ for cyclohexane; $-9.5°$ for cycloheptane, and $-12.75°$ for cyclooctane. The positive values of deviation mean that the bond angles are compressed, while negative values mean expansion of the bond angle from the tetrahedral angle. In both the situations the molecule would be strained.

Thus, Baeyer predicted that a five membered ring compound would be the most stable. He predicted that six membered ring compound would be less stable and as rings became larger than five membered ring they would become less and less stable.

Contrary to what Baeyer predicted, cyclohexane is more stable than cyclopentane. Furthermore, cyclic compounds do not become less and less stable as the sides in their ring increase.

Thus, Baeyer strain theory is applicable only to cyclopropane, cyclobutane and cyclopentane. The mistake that Baeyer made was to assume that all cyclic compounds are planar. In real sense only cyclopropane is planar and other cycloalkanes are not planar.

Cyclic compounds twist and bend in order to achieve a final structure which minimises the following three kinds of strain that can destabilise a cyclic compound :

1. **Angle strain (Baeyer strain) :** This results when the bond angle is different from the desired tetrahedral bond angle of 109.5°.

2. **Torsional strain (Pitzer strain) :** This is caused by repulsion of the bonding electrons of one substituent with bonding electrons of another substituent on the adjacent atom.

3. **Steric strain (van der Waals strain) :** This is caused by atoms or groups approaching each other too closely.
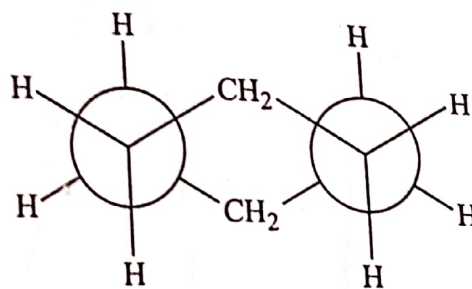
2.27.2 Conformations of cyclohexane

Sachse (1890) proposed that cyclohexane and larger rings are not planar but they are puckered in which all the angles are tetrahedral, and thus, the rings are strainless. According to Sachse cyclohexane exists in two forms which are called the **chair** and **boat conformations.** Mohr (1931) suggested the possibility of existence of two forms which readily undergo interconversion by rotation about single bonds. This theory is known as Sachse-Mohr theory of strainless rings.

Both the chair and the boat forms are free from angle strain. In the boat conformation the C—H bonds at C_2, C_3 and C_5, C_6 are eclipsed resulting in torsional strain, while in the chair conformation all the C—H bonds on adjacent carbons are staggered. Furthermore, in the boat conformation there is steric repulsion between the two hydrogens (flagpole hydrogens) pointing towards each other at C_1, and C_4, and lying only 1.83 Å apart (closer than the sum of their van der Waals radii, 2.5Å). This causes steric strain. Hence, the total strain in the boat conformation is larger than that in the chair
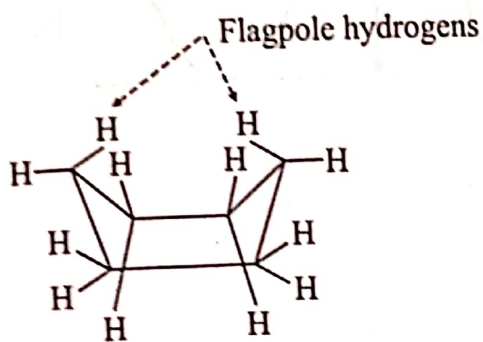
conformation because the latter is free from torsional and steric strains. Thus, the chair conformation is more stable than the boat conformation.
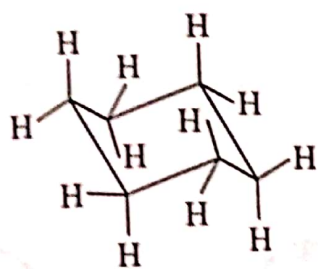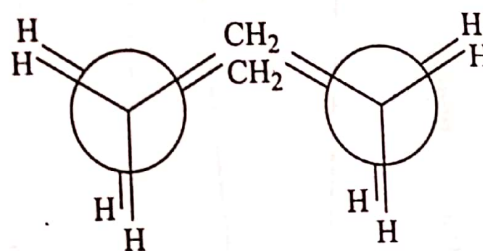

Chair conformation
of cyclohexane

Newman projection
of the chair conformation

Flagpole hydrogens

Boat conformation
of cyclohexane

Newman projection
of the boat conformation

The chair conformation is rigid because when it is changed to the boat conformation, some angular deformation is necessary. The energy barrier for this transformation is 10.8 kcal/mole. The energy barrier is not large enough to prevent interconversion of the chair and boat conformations at room temperature, but is large enough for the existence of each conformation.

The boat conformation is flexible and can be readily distorted into many shapes in which the eclipsing of C—H bonds is reduced. In a modified boat conformation, known as the twist boat, the torsional and steric strains are minimized (Fig. 2.7).
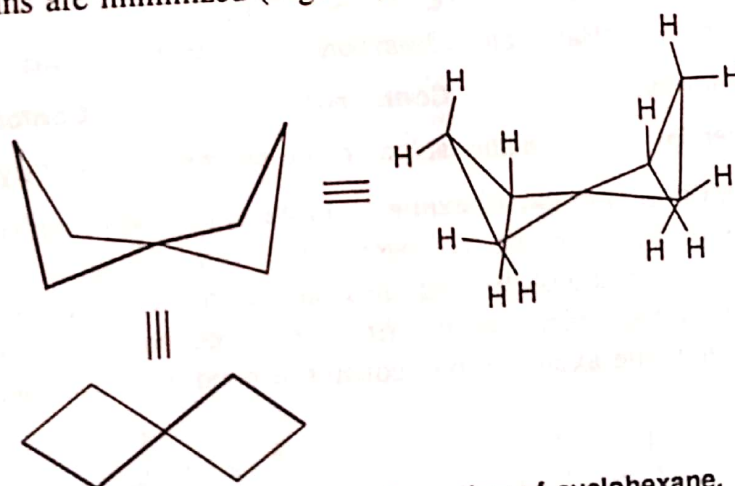

Fig. 2.7. Twist boat conformation of cyclohexane.

The twist boat is about 1.5 kcal/mole lower in energy than the boat form at 25°C. At room temperature, most of cyclohexane molecules (99.9%) exist in the most stable chair conformation. The twist form occurs as an intermediate stage in the conversion of one chair form to another (Fig. 2.8). Since the boat form is preferred conformation only in a few cases, we shall confine our attention to the chair form.
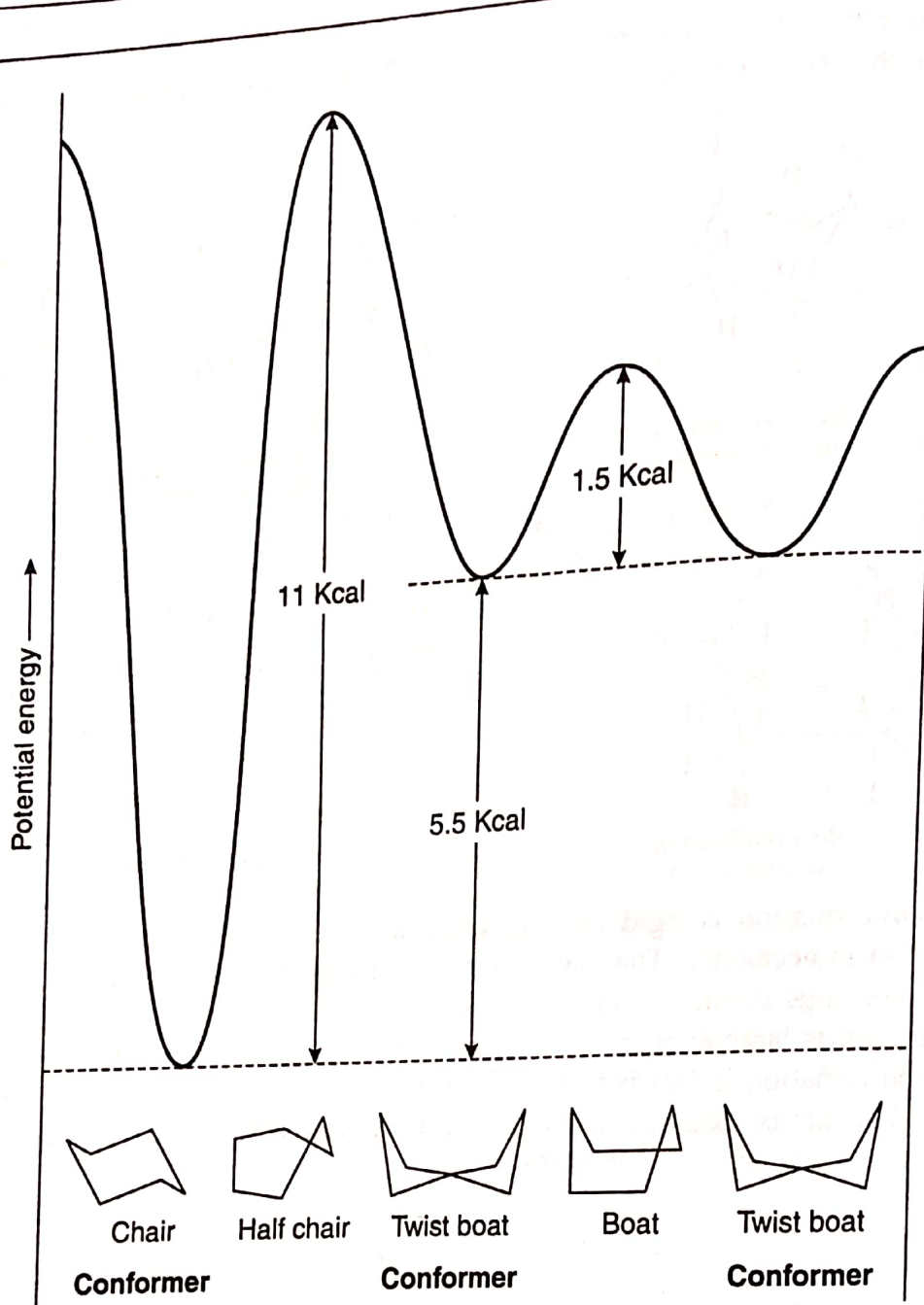
Fig. 2.8.   Potential energy relationships among conformations of cyclohexane.

Axial and equational bonds in cyclohexane :   In the chair conformation of cyclohexane, there are two kinds of positions occupied by the hydrogen atoms. Six hydrogens are held by bonds which are perpendicular to the average plane of the ring; these are called axial (*a*) bonds. The other six bonds holding hydrogens in the average plane of the. ring are called equatorial. (*e*) bonds. In the chair conformation each carbon has one axial and one equatorial bond as shown below :
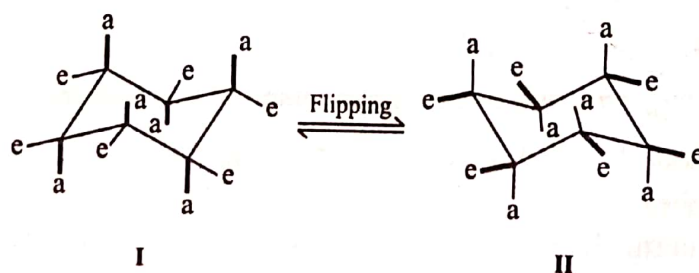
At room temperature cyclohexane rapidly interconverts (flips) to mirror image chair conformations. On flipping all the equatorial hydrogens become axial and all the axial hydrogens