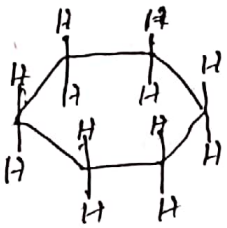
PROF. (DR) D. N. THAKUR
HEAD, P. G. DEPARTMENT OF CHEMISTRY,
PATNA UNIVERSITY
PATNA

Topic for the M.Sc. IInd semester students
PAPER – CC VII (CBCS)

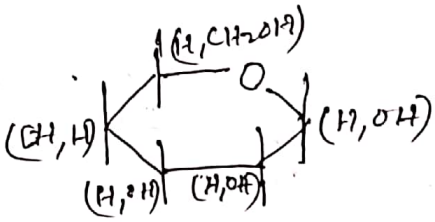
Conformation of monosacchides and their derivatives

As hexoses and pentoses are naturally occuring monosacchrides, we can consider either the δ-oxide rings (Pyranose ring) or the γ-oxide rings (Furanose ring) in order to express their conformation.

If we want to give a clear cut picture of conformation due to the Pyranose ring, a comparison with the cyclohexane ring is essential.



cyclohexane

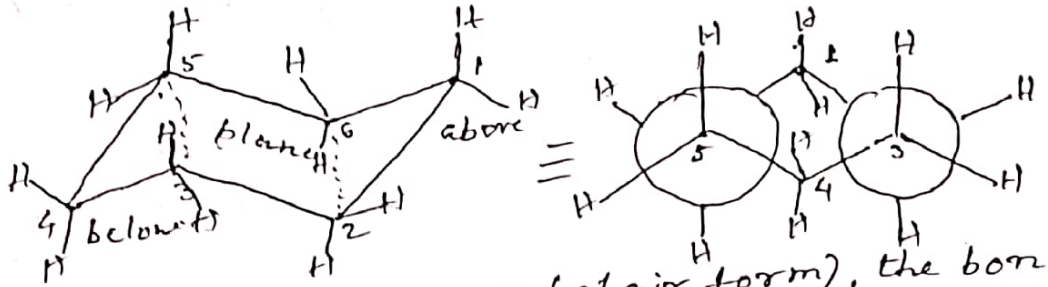


Haworth Projection

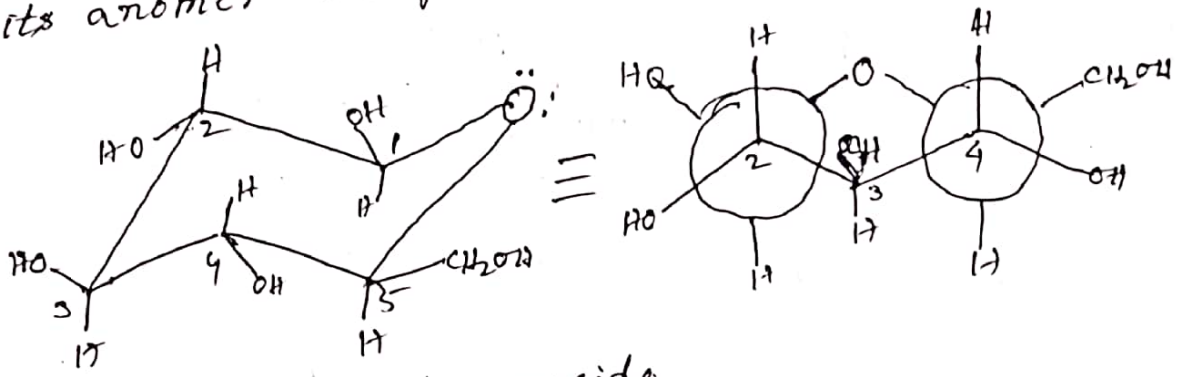
The molecules will not exist if the rings are planar (flat), mainly due to the angle strain and torsional strain. In the planar form, the bond angles ($\begin{matrix}C\\C\end{matrix}\!\!>\!\!C$ or $C\!\!>\!\!O$) are 120°, whereas the single bonded carbon for the minimum energy state will try to maintain the tetrahedral angle (109.5°). This will be the cause of the angle strain (Baeyers strain) in the planar form. The torsional strain in the ring are mainly due to the eclipsing of bonds of the neighbouring carbon.

Hence for the minimum energy state for these ring systems, puckering in the ring is imagined.

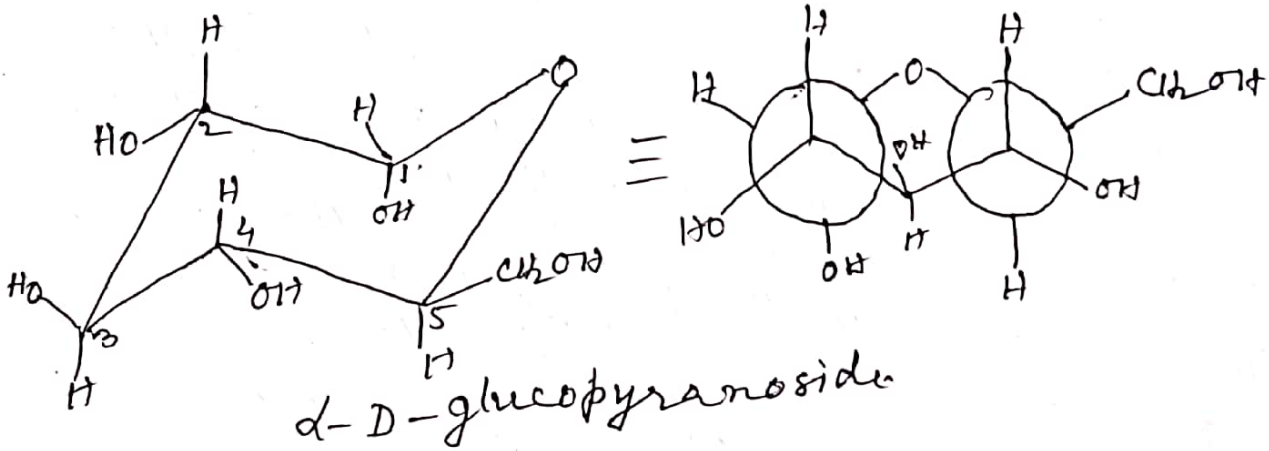
(2)



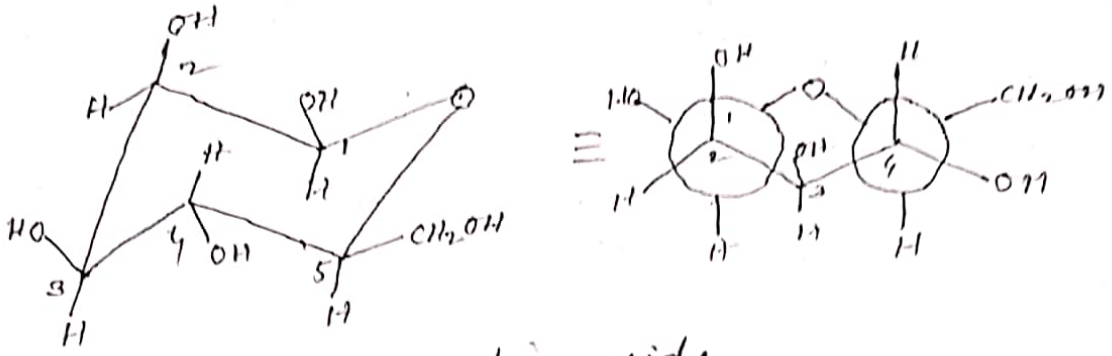
In this puckered form (chair form), the bond angles are 109.5° (Angle strain = zero) and the torsional strains are also absent due to the staggered form of conformation between the neighbouring carbons. Taking the reference of the chair form of cyclohexane, we can propose the chair forms of glucopyranose along with its anomer and epimers.



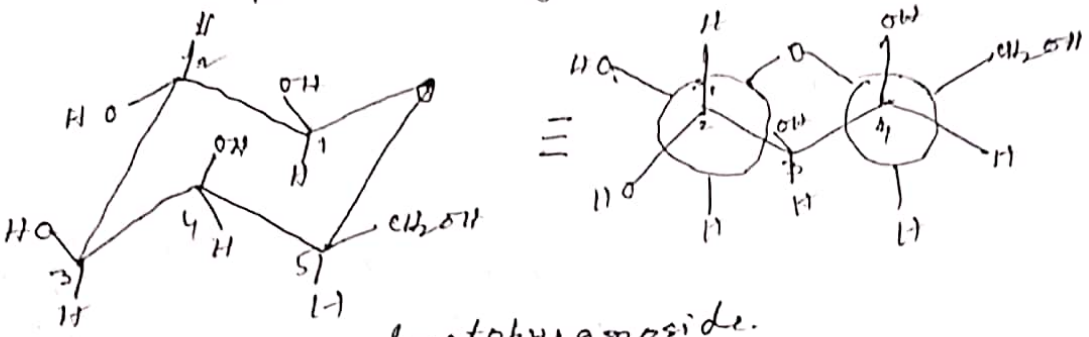
β-D-glucopyranoside



α-D-glucopyranoside

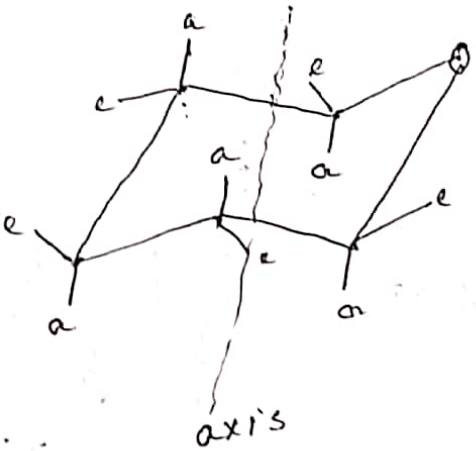


β-D-mannopyranoside



β-D-glactopyranoside.

In the chair conformation, the two exocyclic atoms/substituents of a ring carbon atom are not geometrically/chemically equivalent. One is parallel to the axis of the pyranose ring (axial bond ≡ a) and another is perpendicular to this axis (equitorial bond ≡ e).



The spatial distance between the atoms/substituents on the carbon atoms of the ring is normally greater than their Vander Waal's radii and therefore the molecule is nearly free from any torsional strain (this statement is perfectly true of atoms are H's)

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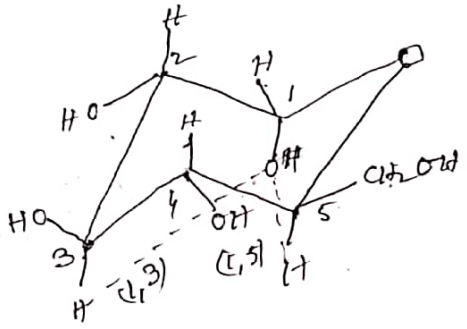
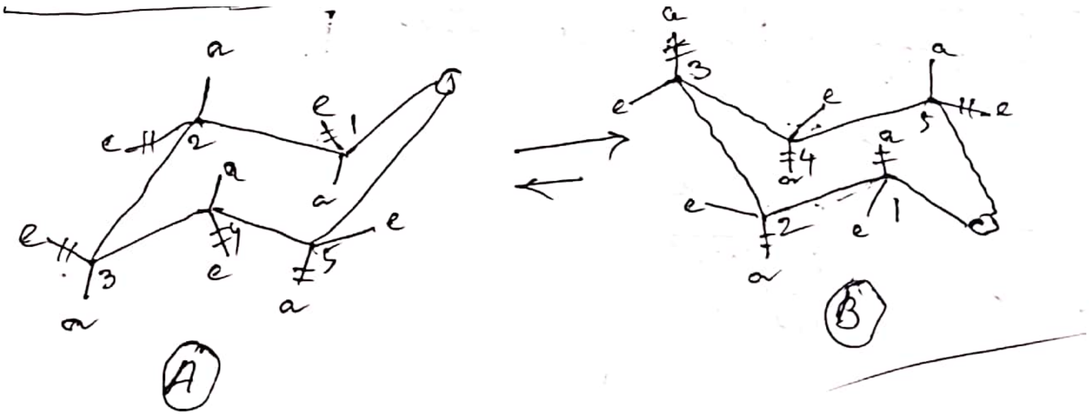
With the increase in the volume (size) of the substituents, their spatial distance decreases and the non-bonded interaction (torsional strain) increase. Normally this effect is common when a substituent is axially present and this is known as 1,3 – & 1,5 interactions. In the case of the substituents at equitorial position, the effect is nearly negligible.



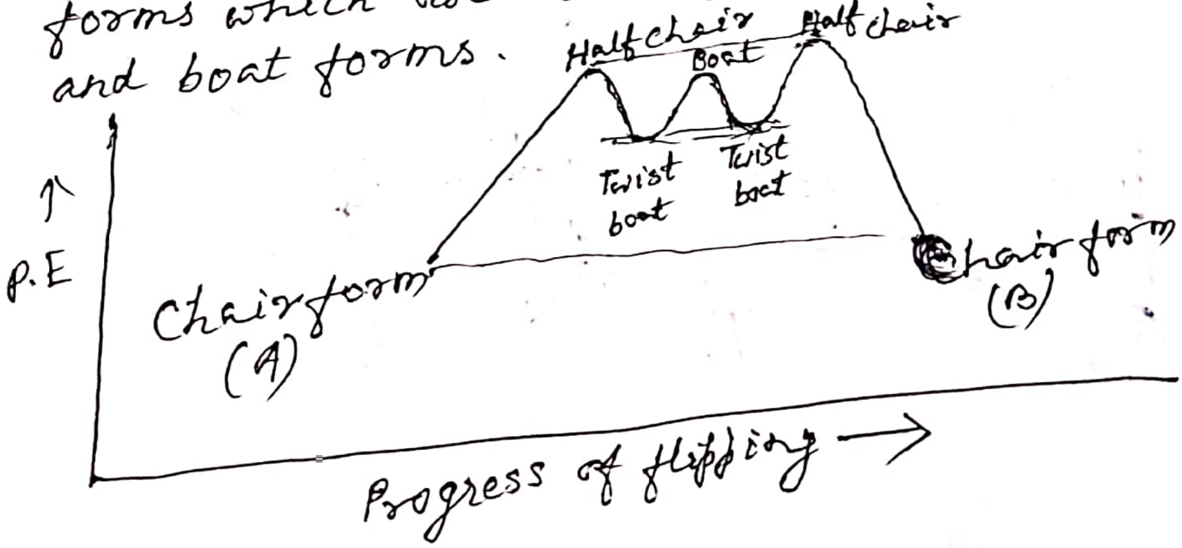
The conformation of cyclohexane/pyranose ring is slightly different from the conformation of ethane/n-butane. In the case of the acyclic system, the rotation around carbon-carbon single bond is easier and therefore the energy barrier is low (~3.0 KJ/mole).

But In the case of cyclohexane/pyranose ring, the rotation around the single bond is slight restricted (indicated by high energy barrier, rigid system). This rotation effects many bonds of the ring and it is known as flipping.

Due to the flipping of the bonds, one chair form of the ring is converted into its another chair form. It was found that the axial substituents of the ring acquire equitorial position in another form and vice-versa.



When the form (A) is converted into the form (B), the ring will acquire very high energy intermediate forms which are identified as half-chair, twist boat and boat forms.



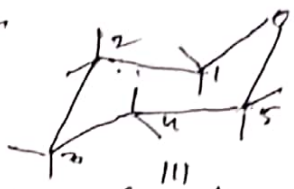
When a chair is converted into half-chair, the bond angle at the corner and the neighbouring carbons is disturbed which suddenly increases the energy of the molecule (energy peak).

The molecule suddenly changes its shape into twist boat in order to get relief from the angle strain (bond angle ~ 109°28') but in this form eclipsed interactions will push the molecule into the higher energy state.

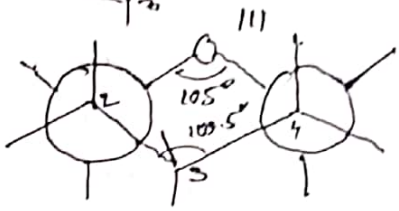
The conversion of the twist boat into the boat form, the flag pole interaction is enhanced in addition to the eclipsed interaction, which will increase the energy of the ring.

The conversions can be expressed as :→

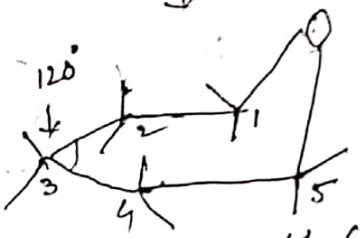
chair form into the Half-chair as :-



chair form

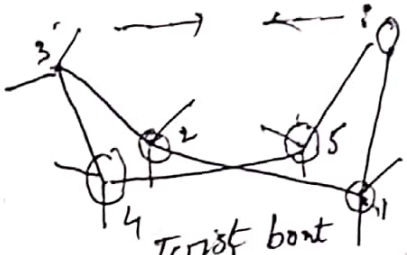


All staggered and the normal bond angles of ring atoms are maintained



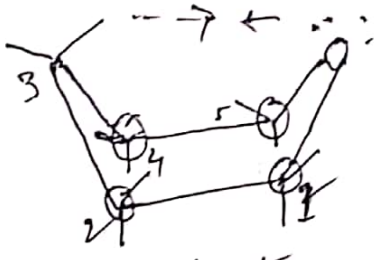
angle strain.

Half chair

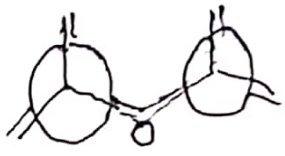


Twist boat

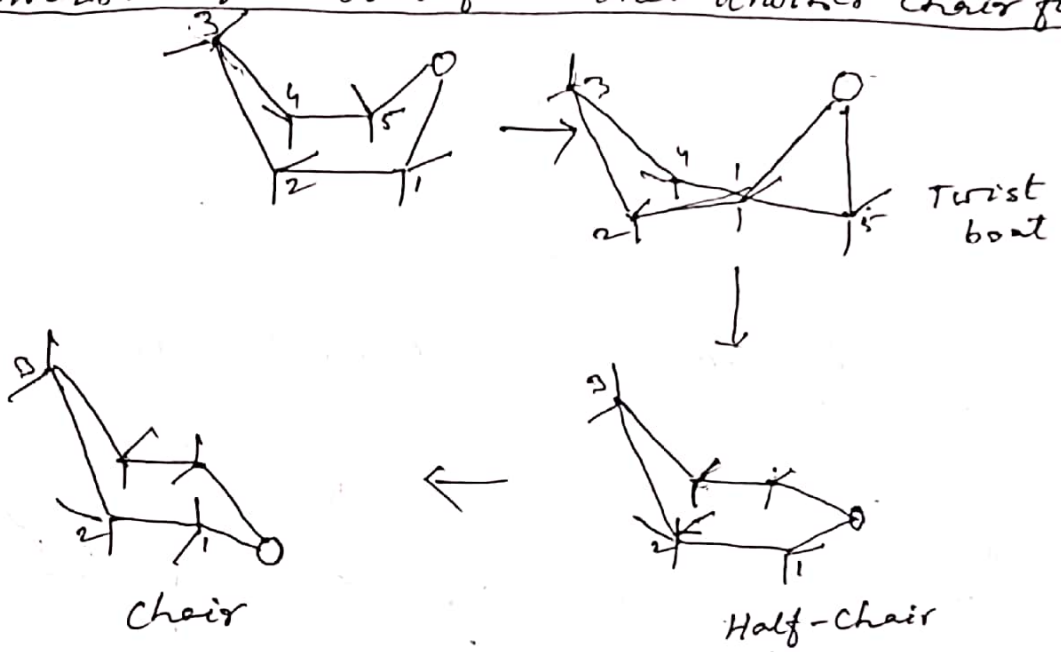
stability increase because of the relief from the angle strain but eclipsed interaction is expected



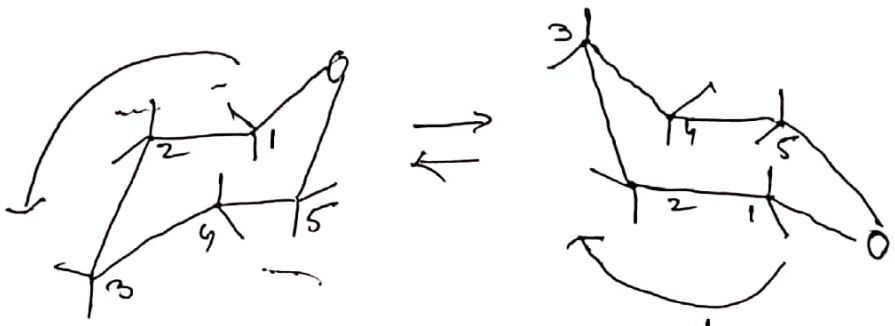
boat



Conversion of the boat form into another chair form



The two chair forms of the pyranose ring are most frequently encountered in the Carbohydrate chemistry. They can be represented as:



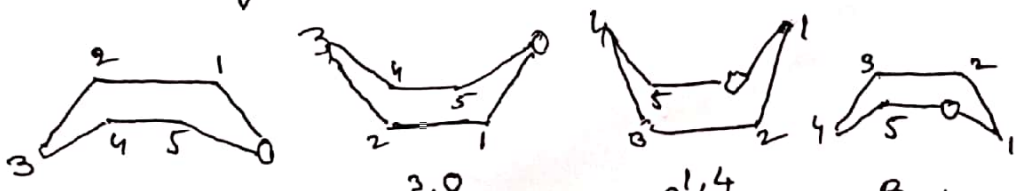
$^{3}C_{0}$

Clockwise numbering increases

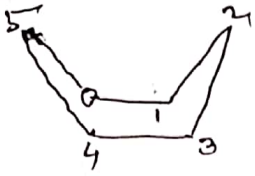
$^{0}C_{3}$

Anti-clockwise numbering increases.

A total of six boat conformations are possible for the pyranose rings depending upon which pair of atoms are puckered out of the boat plane and on whether they are above or below.



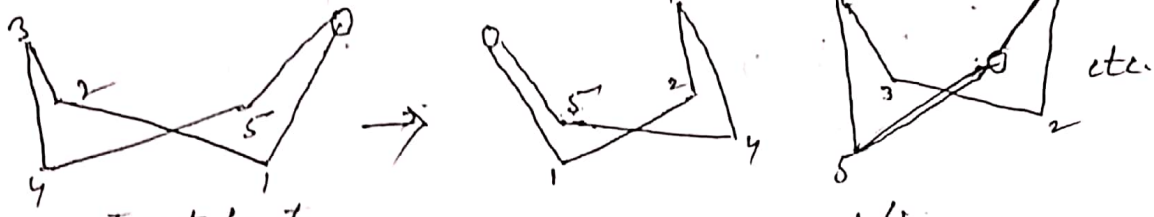
$^{2,5}B$ $B^{3,0}$ $B^{1,4}$ $B_{1,4}$



$B^{2,5}$

$B_{2,5}$

We can also imagine six twist boat form for the pyranose ring.



Twist boat or Skew boat

$T^{0,3}$, $T^{1,4}$ etc.

continued in the next class