

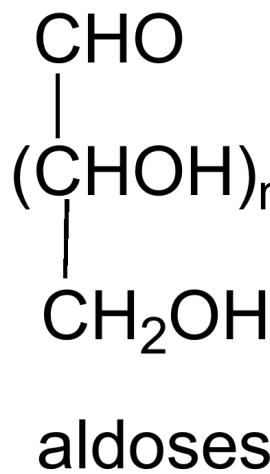
Open chain and ring structures of monosaccharides

1. Aldoses and ketoses: open chain structures

Empirical formula CH_2O (hydrated carbon)

Contain an oxygen atom attached to each carbon

Highly functionalized

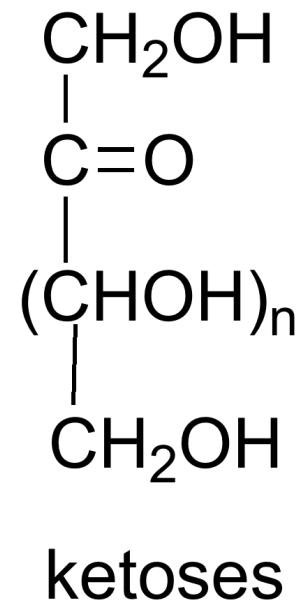


Linear carbon chain

Aldehyde at C-1

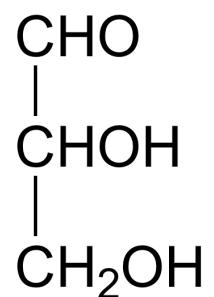
Various secondary alcohol

A primary alcohol at the end

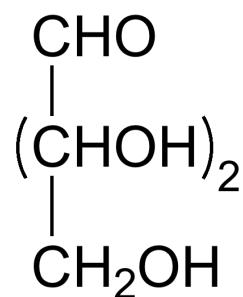


primary alcohols at both ends

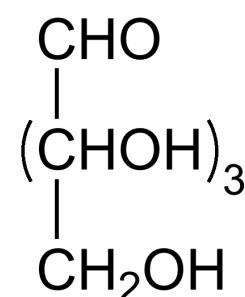
Ketone within the chain



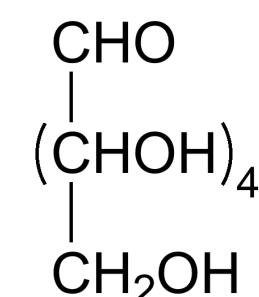
glyceraldehyde



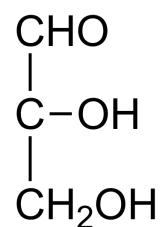
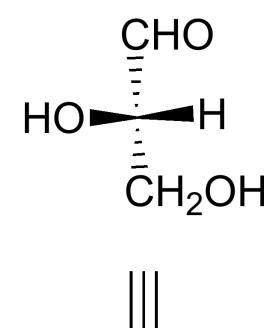
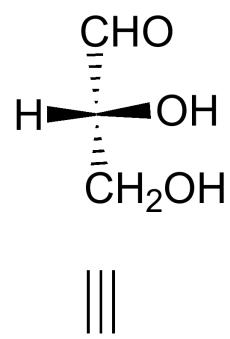
tetrose



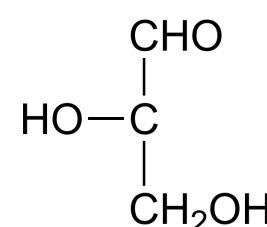
pentose



hexose



D- or R-



L- or S-

1.1 Erythrose and therose

enantiomers

diastereomers

n CHOH groups, 2^n stereoisomers

configuration

conformation

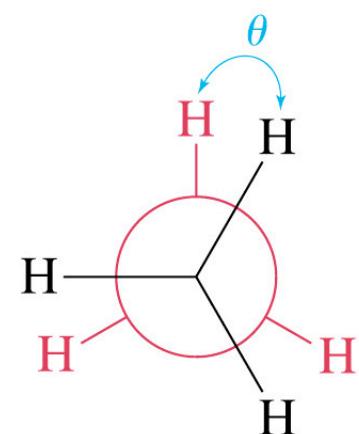
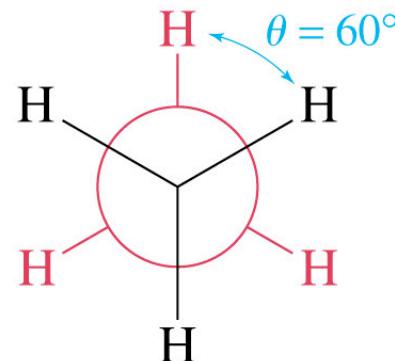
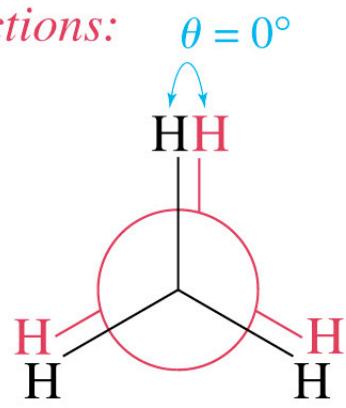
staggered

eclipsed

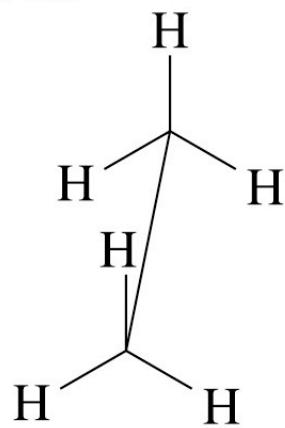
Zigzag drawing

Fischer projection

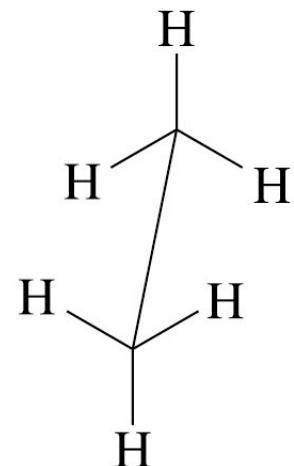
Newman projections:



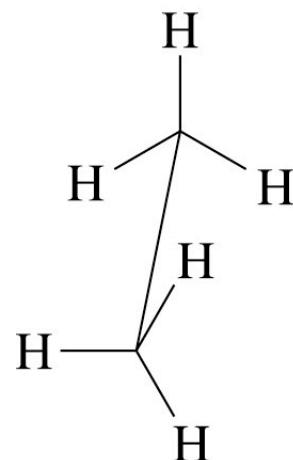
Sawhorse structures:



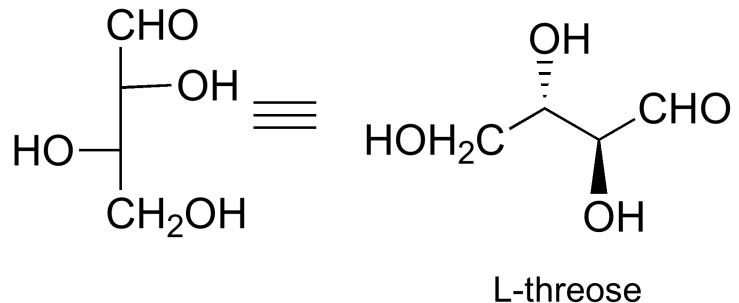
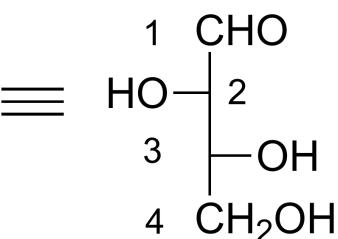
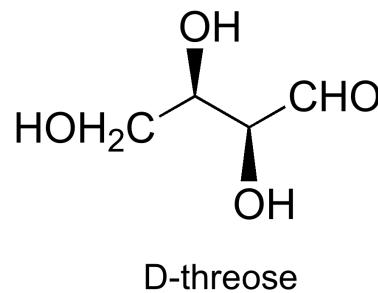
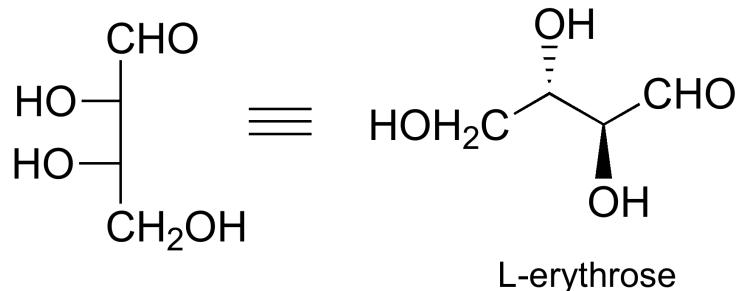
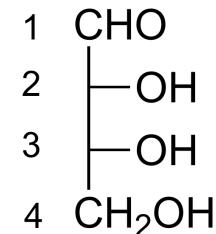
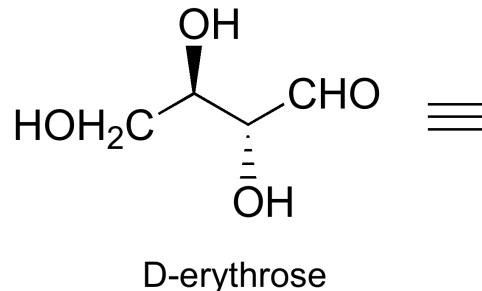
eclipsed, $\theta = 0^\circ$



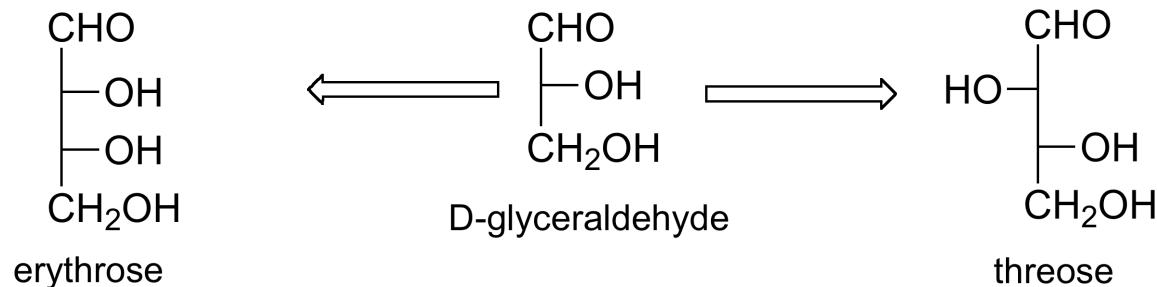
staggered, $\theta = 60^\circ$



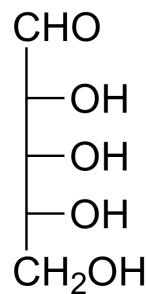
skew, $\theta = \text{anything else}$



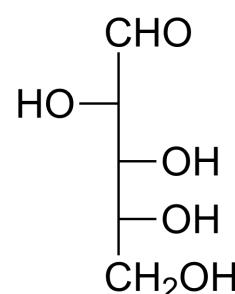
1.2 Pentoses and hexoses



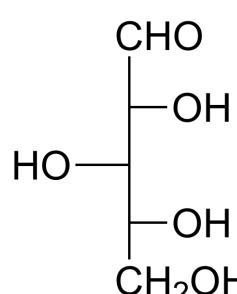
PENTOSES



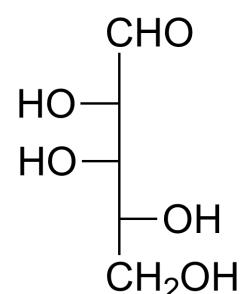
ribose



arabinose

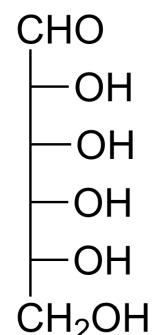


xylose

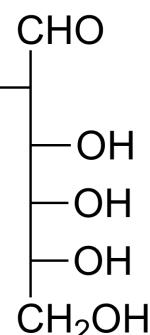


lyxose

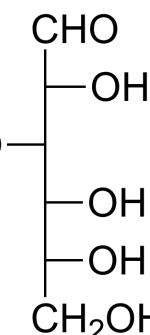
HEXOSES



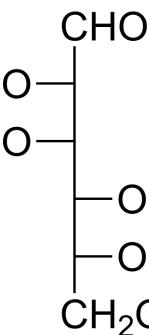
allose



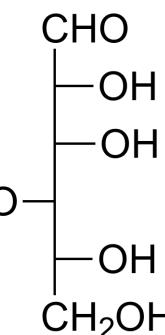
altrose



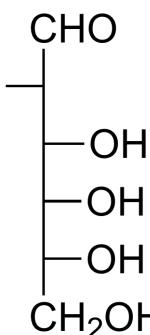
glucose



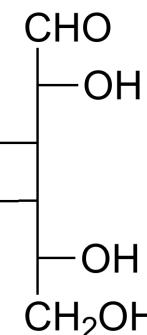
mannose



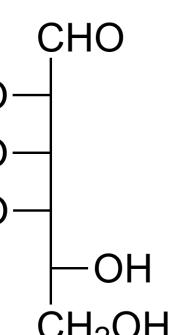
gulose



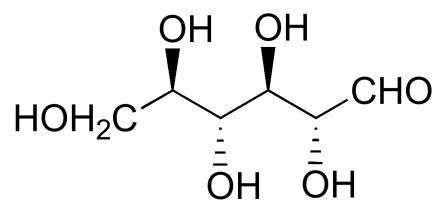
idose



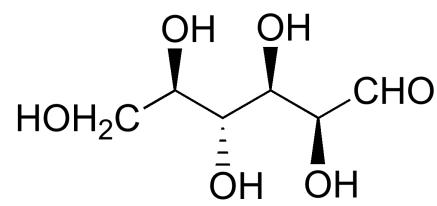
galactose



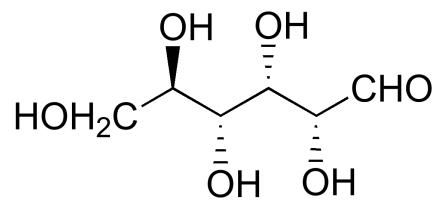
talose



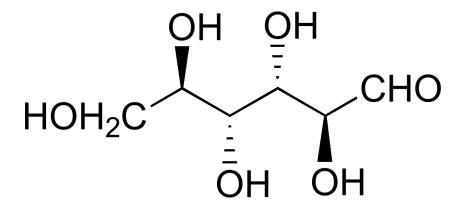
D-allose



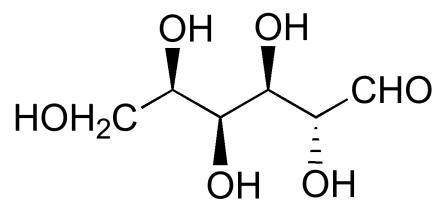
D-altrose



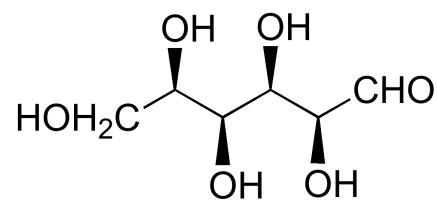
D-glucose



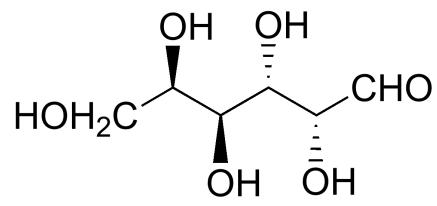
D-mannose



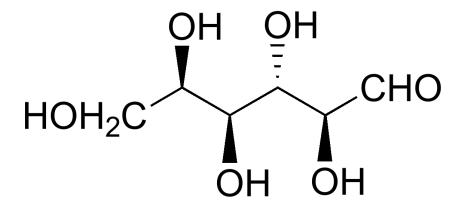
D-gulose



D-idose

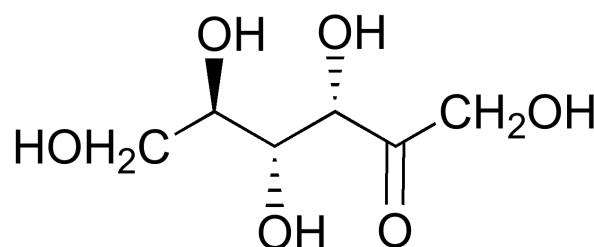


D-galactose

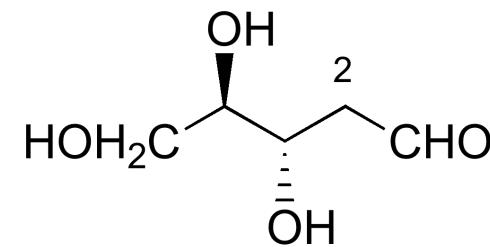


D-talose

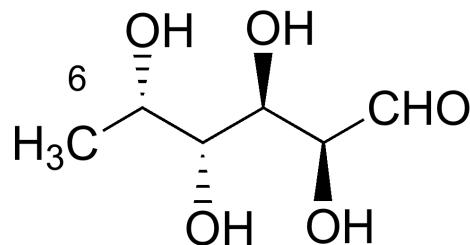
1.3 Other monosaccharides



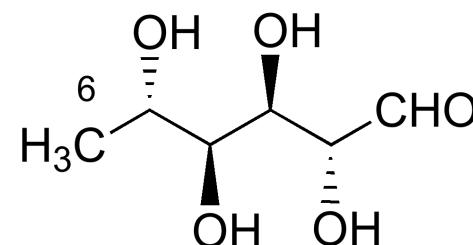
D-fructose



2-deoxy-D-ribose



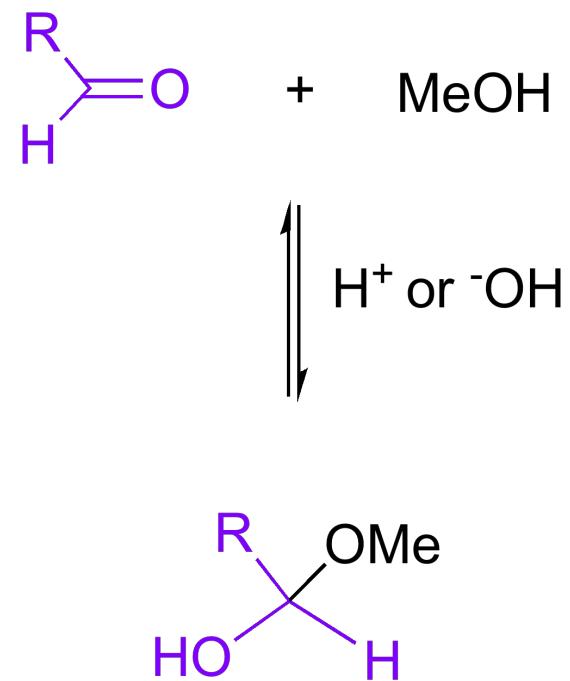
L-fucose



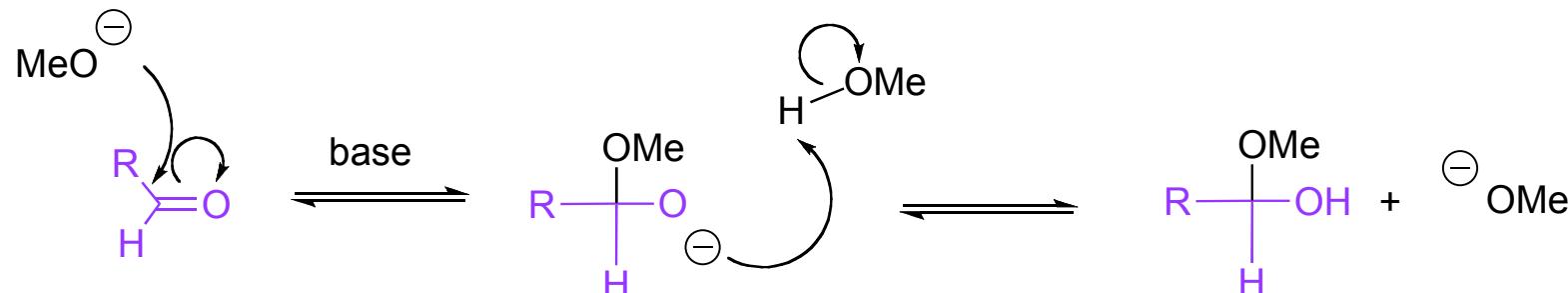
L-rhamnose

2 Ring structure of monosaccharides

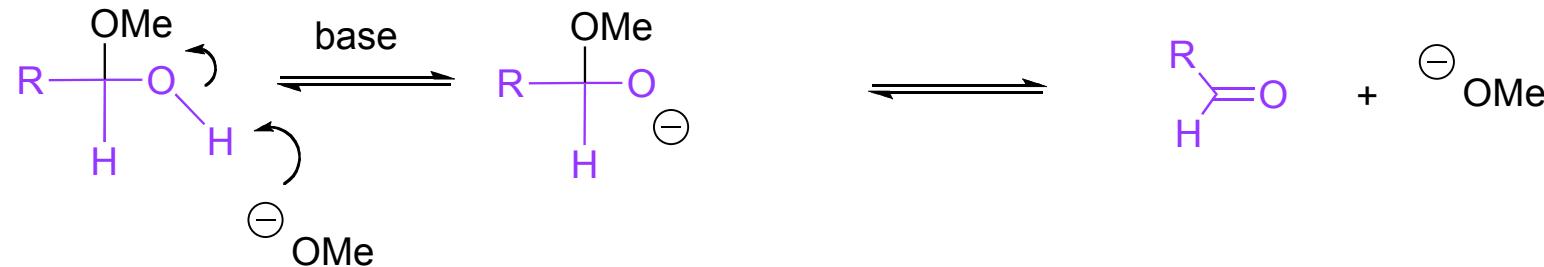
2.1 Hemiacetals and lactols

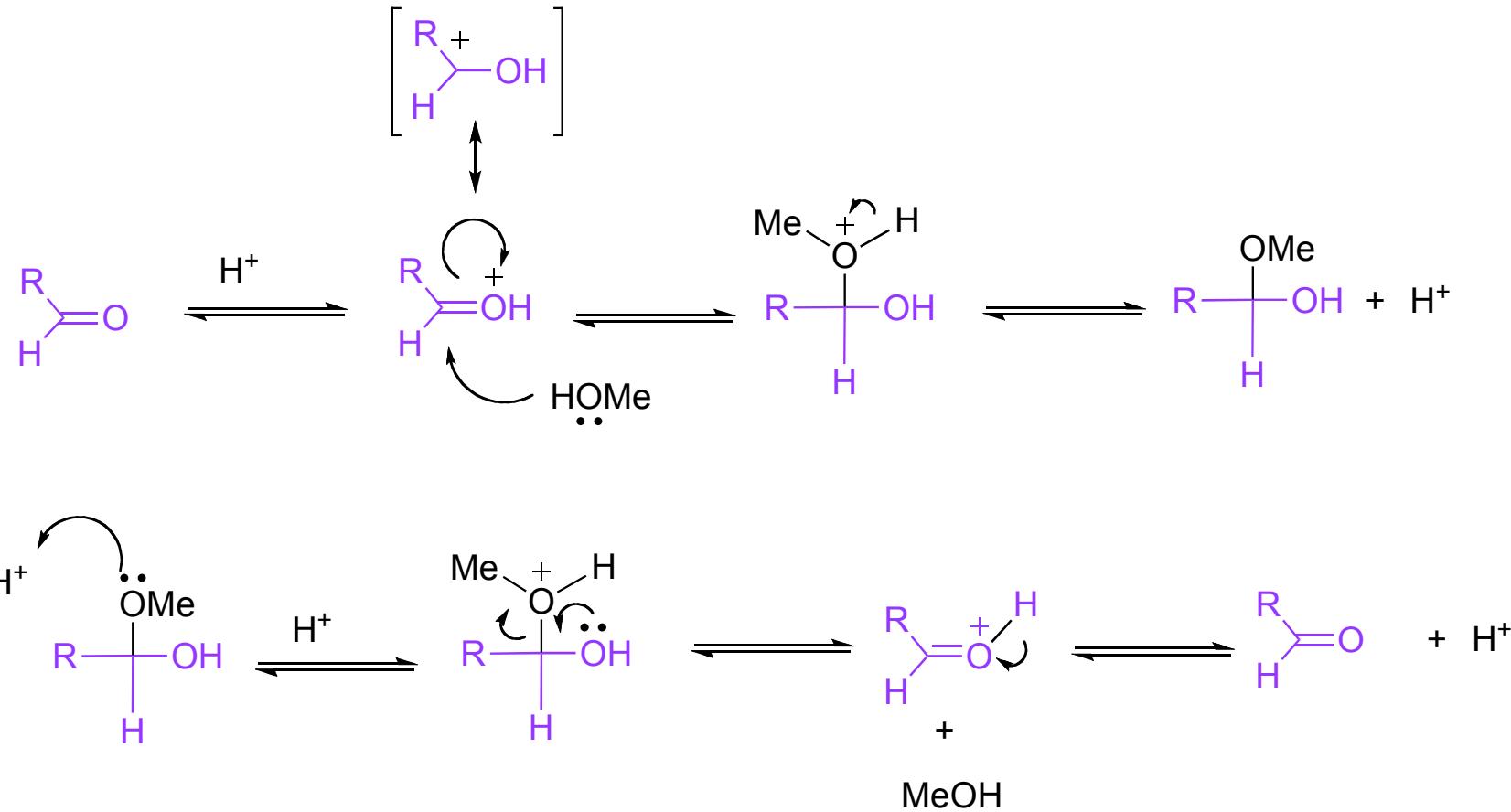


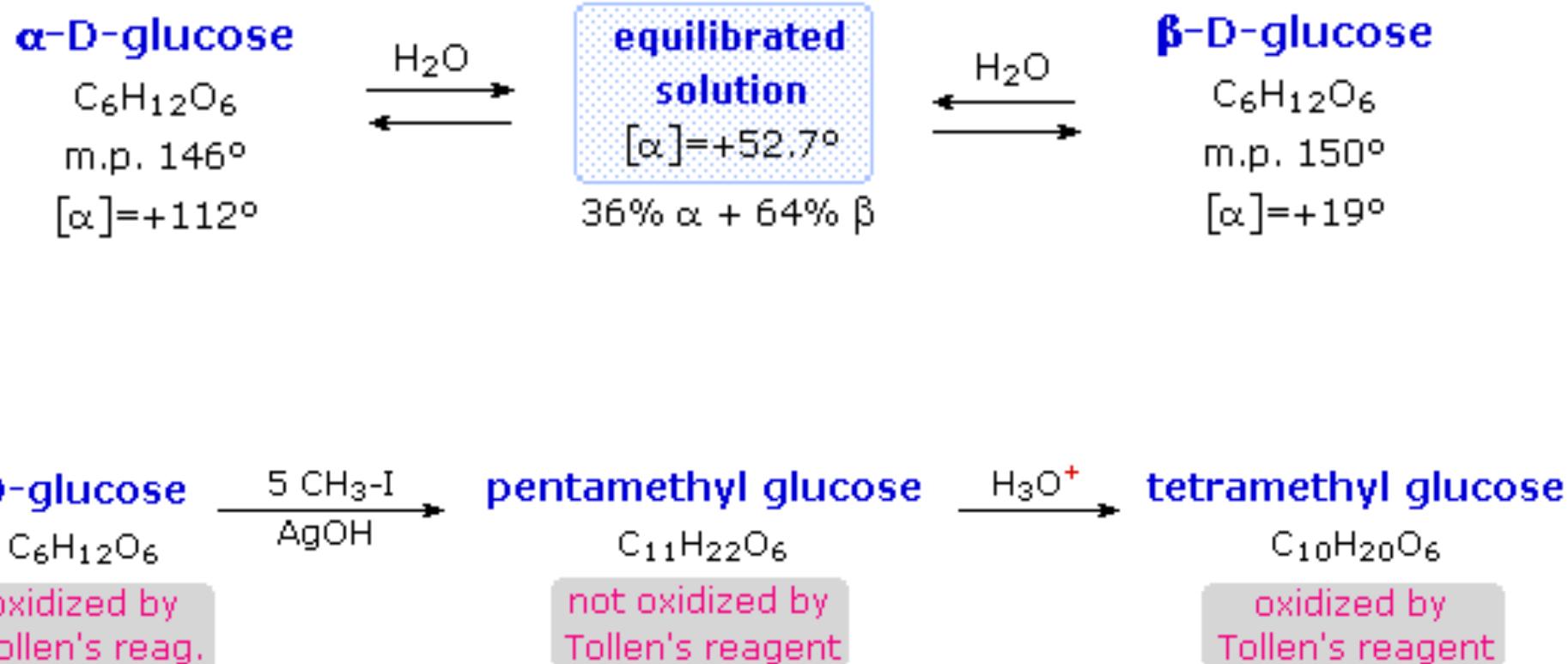
2.2 Mechanism of the reactions

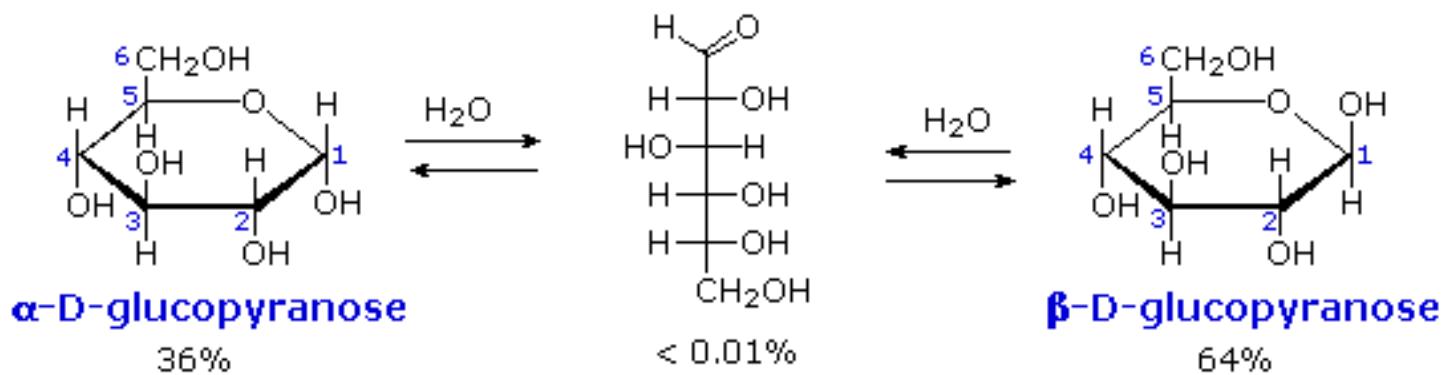
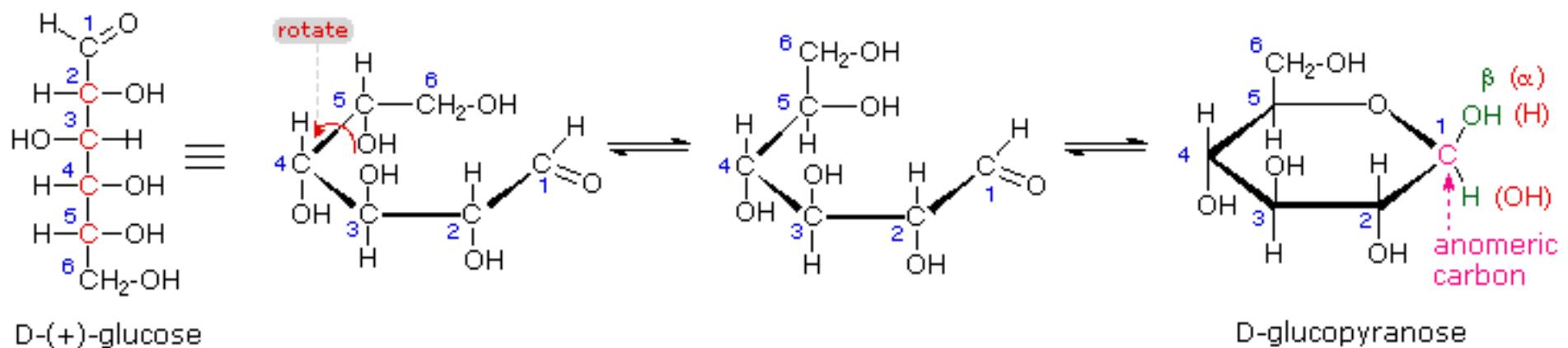


hemiacetal

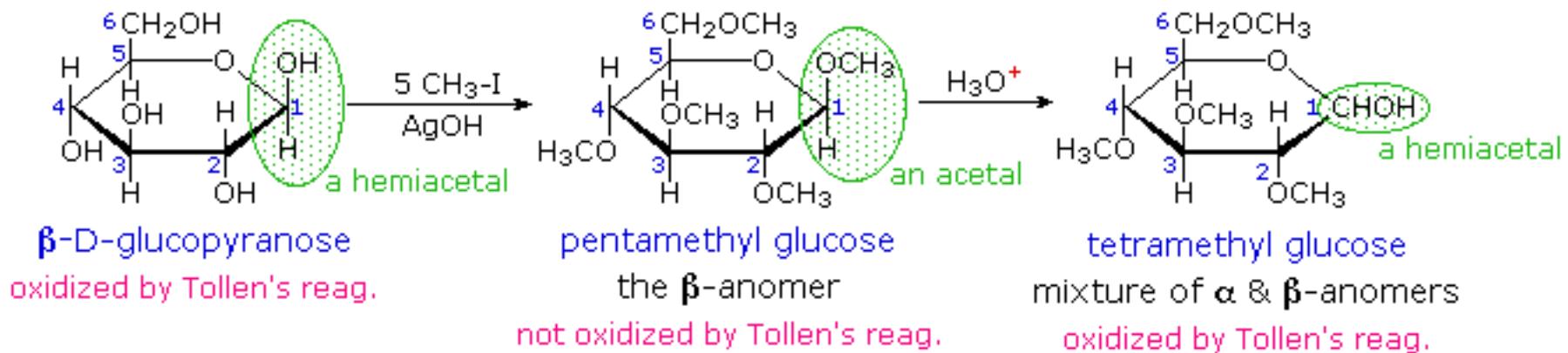




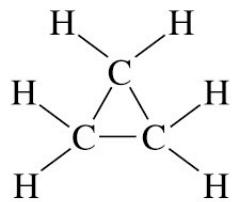




Mutarotation Equilibrium



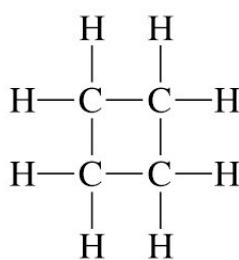
BRIEF REVIEW OF CYCLOALKANES



or



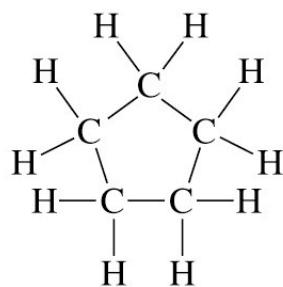
cyclopropane
 C_3H_6



or



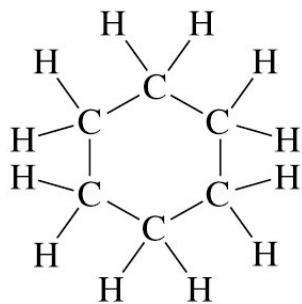
cyclobutane
 C_4H_8



or



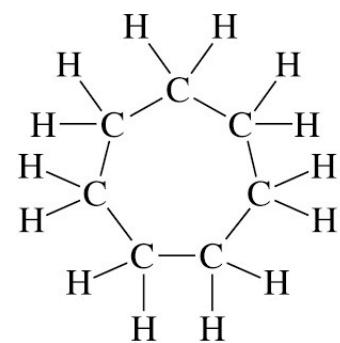
cyclopentane
 C_5H_{10}



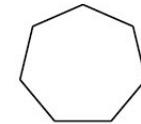
or



cyclohexane
 C_6H_{12}

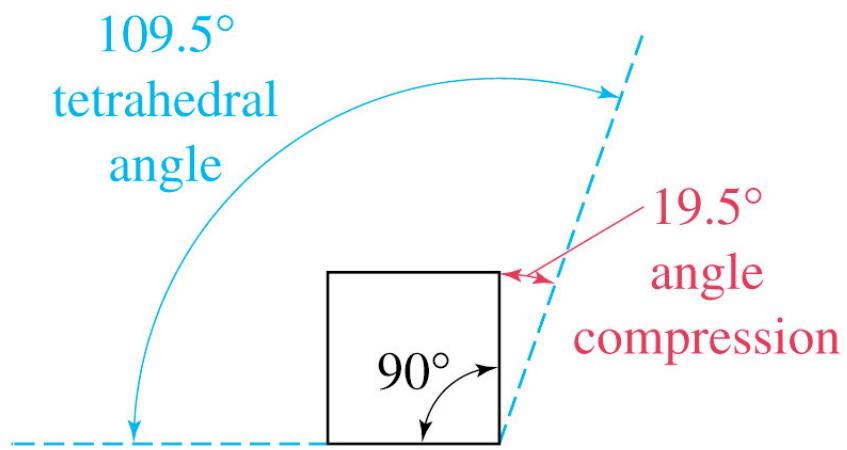


or

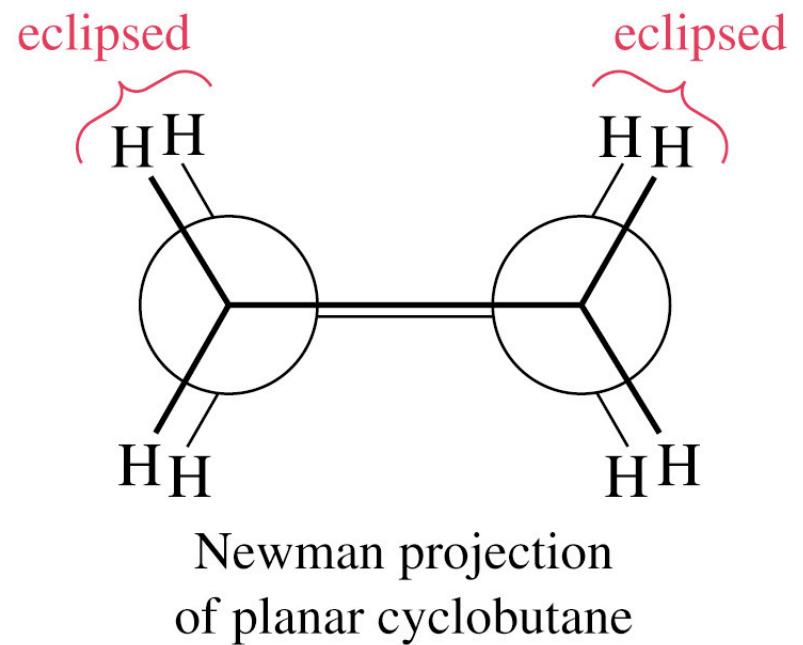


cycloheptane
 C_7H_{14}

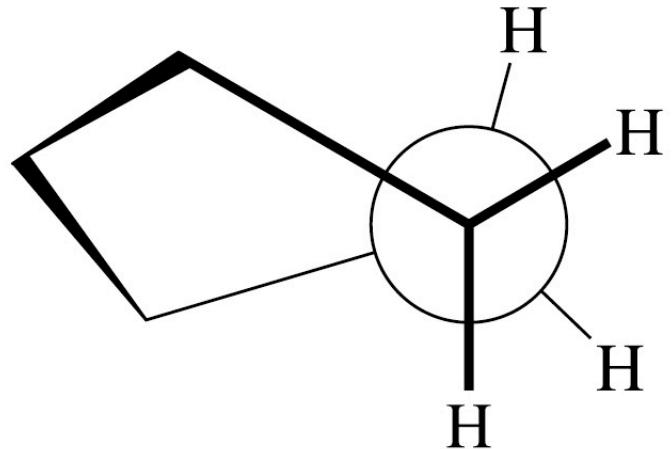
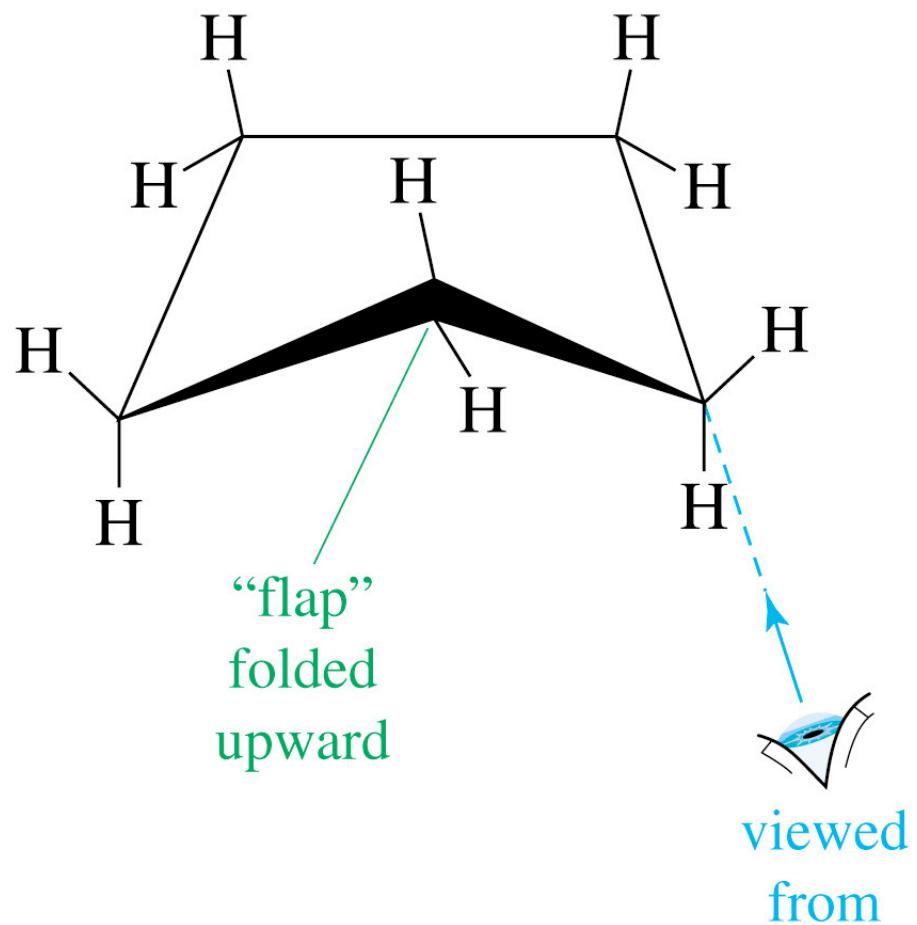
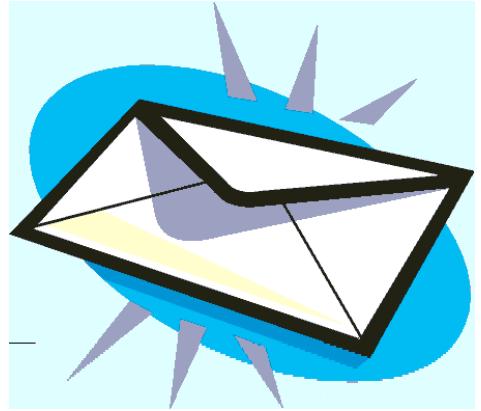
Ring strain



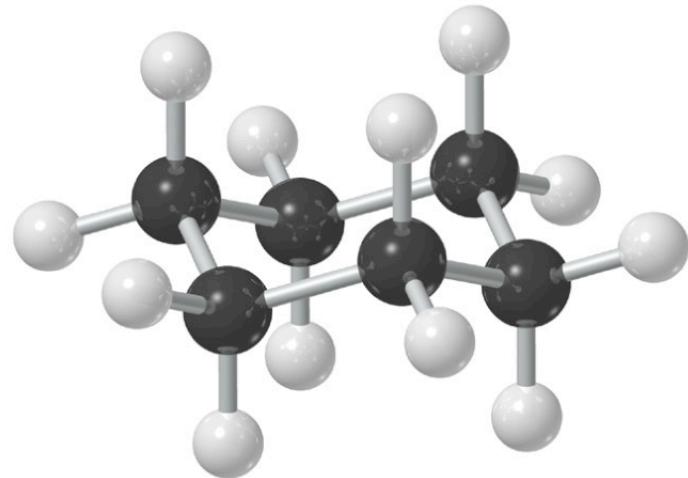
angle strain



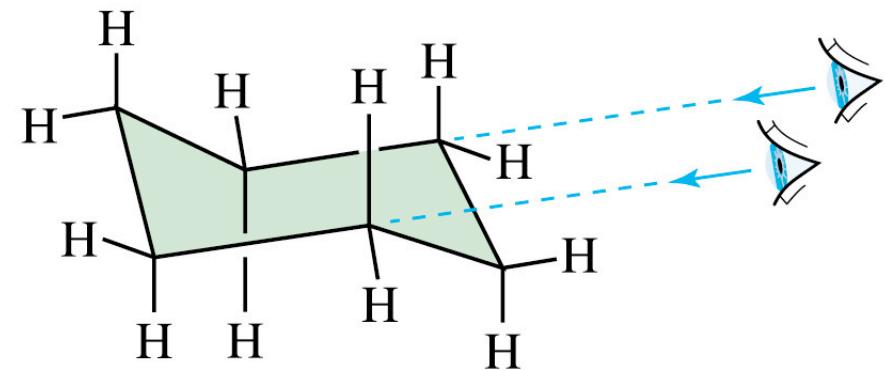
torsional strain



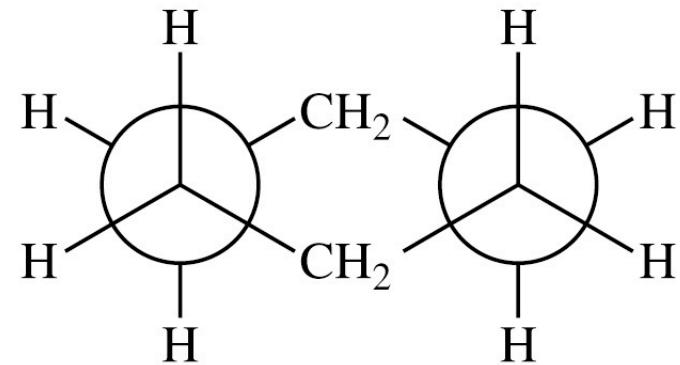
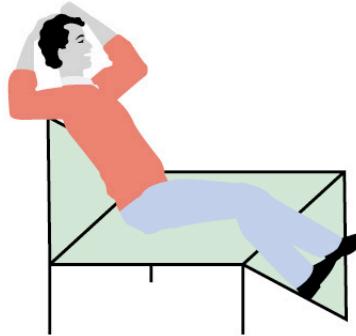
Newman projection
showing relief of
eclipsing of bonds



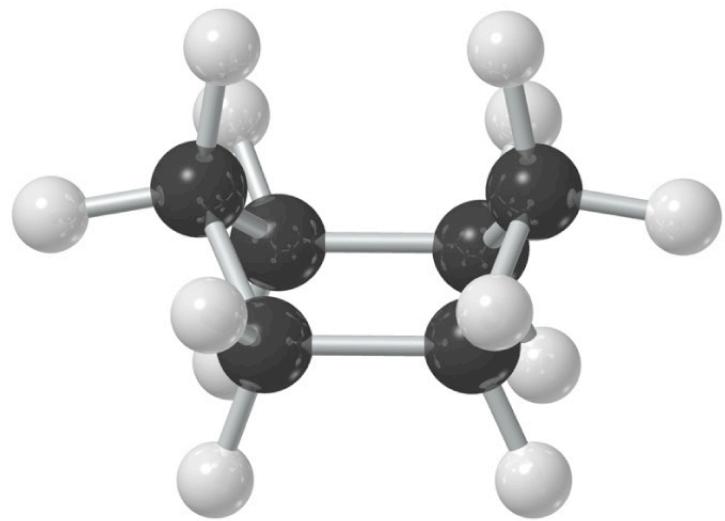
chair conformation



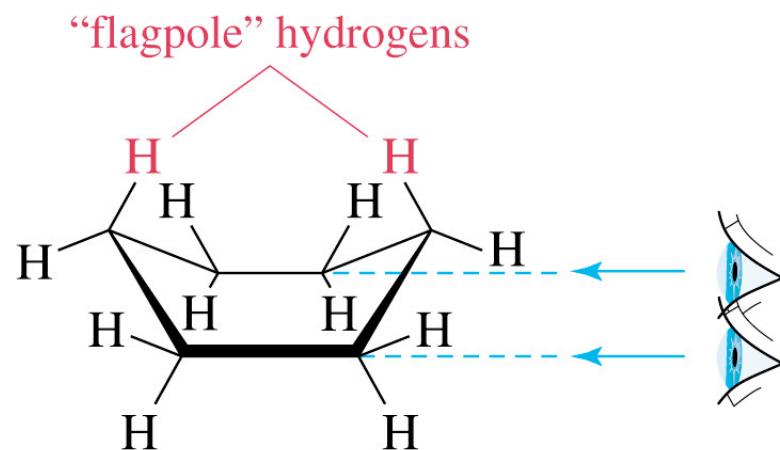
viewed along the “seat” bonds



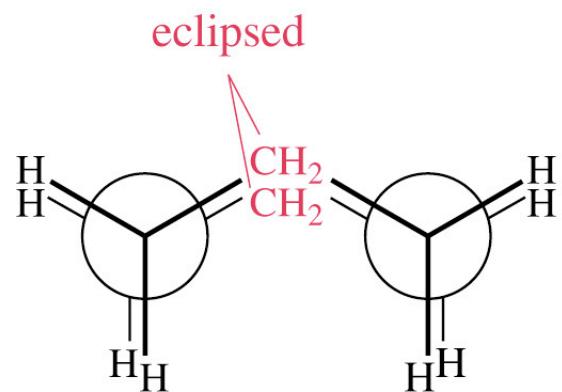
Newman projection



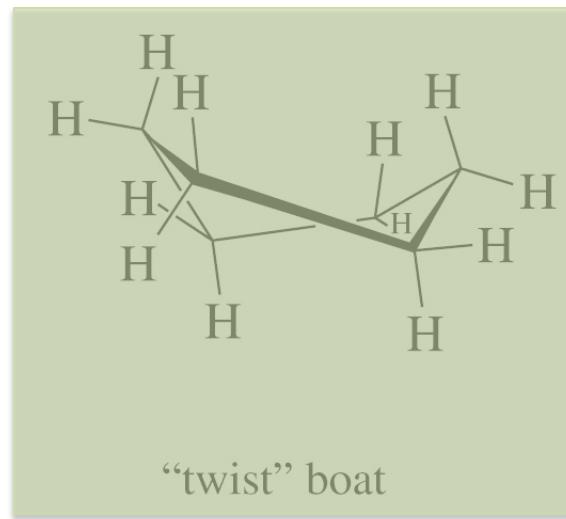
boat conformation



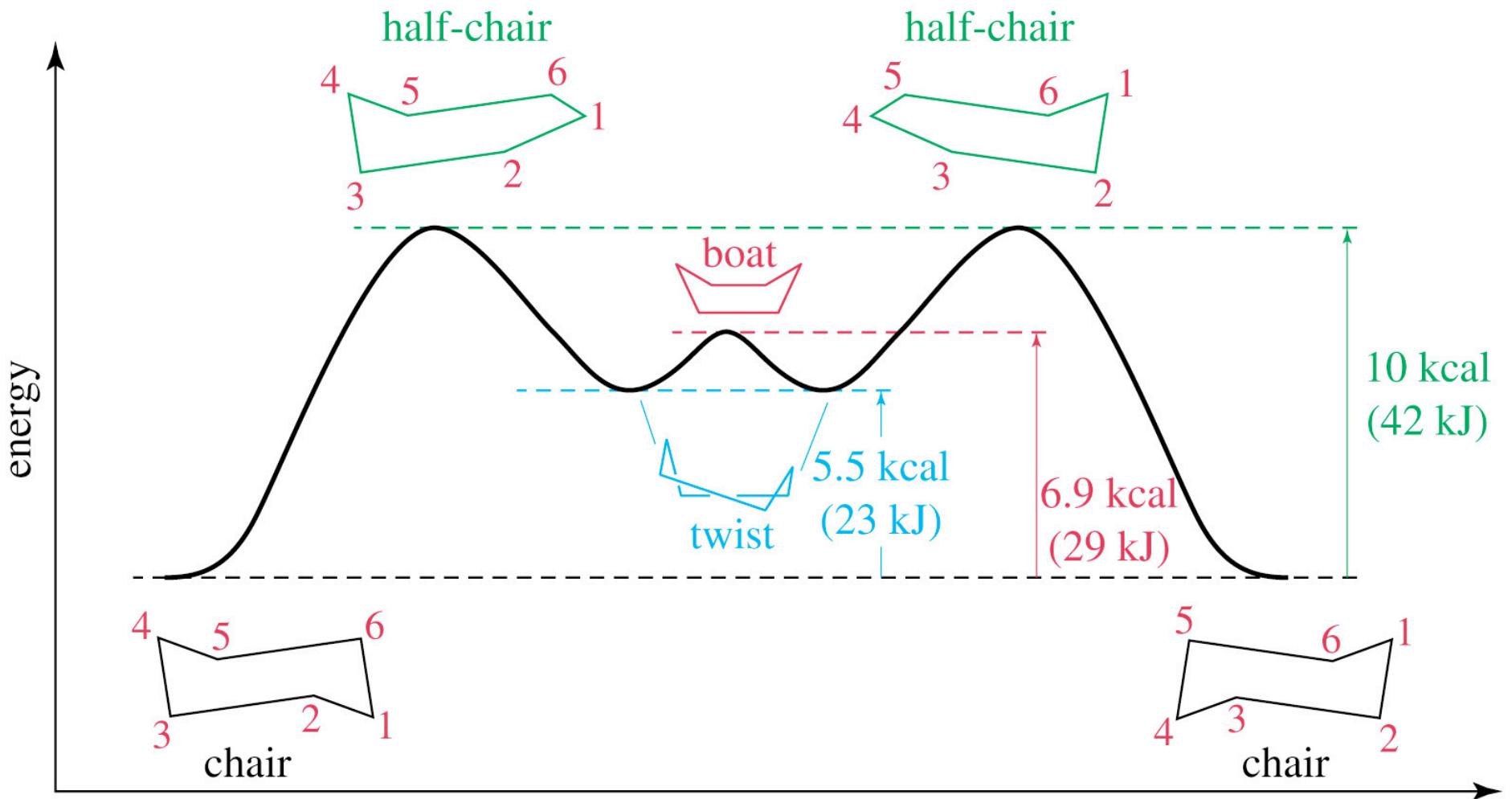
symmetrical boat



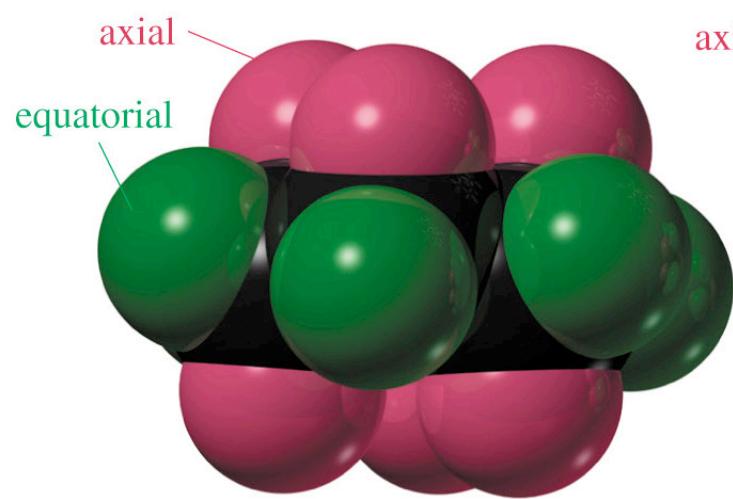
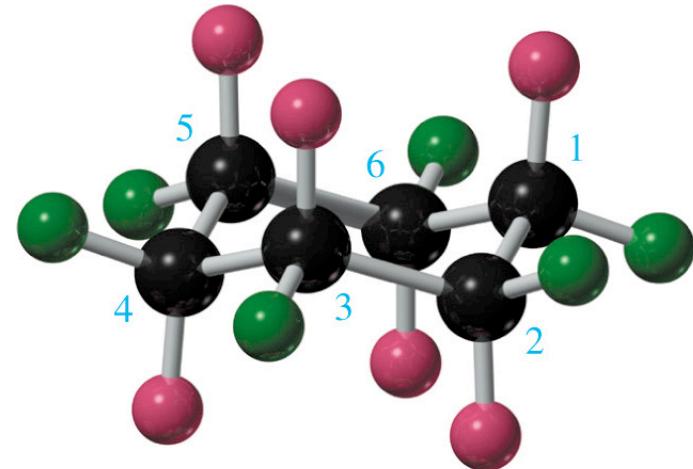
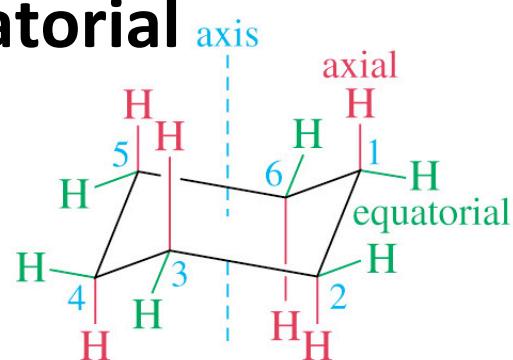
Newman projection



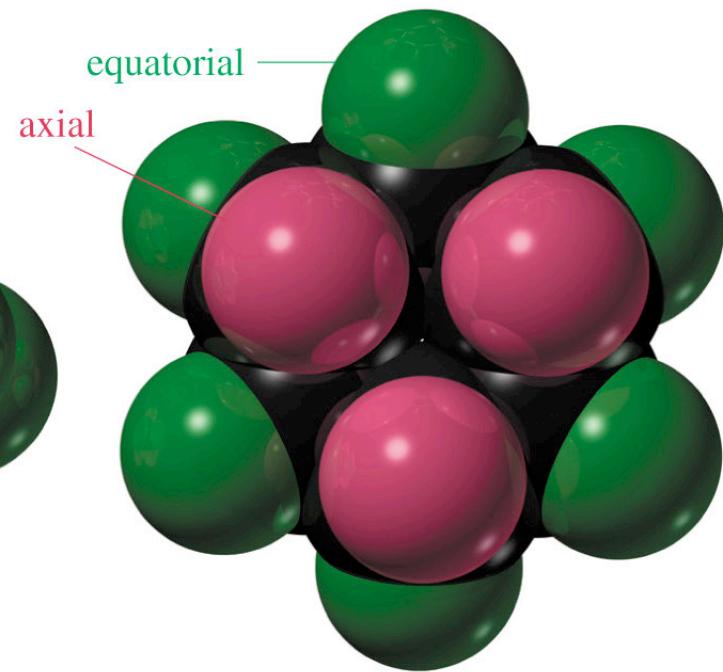
"twist" boat



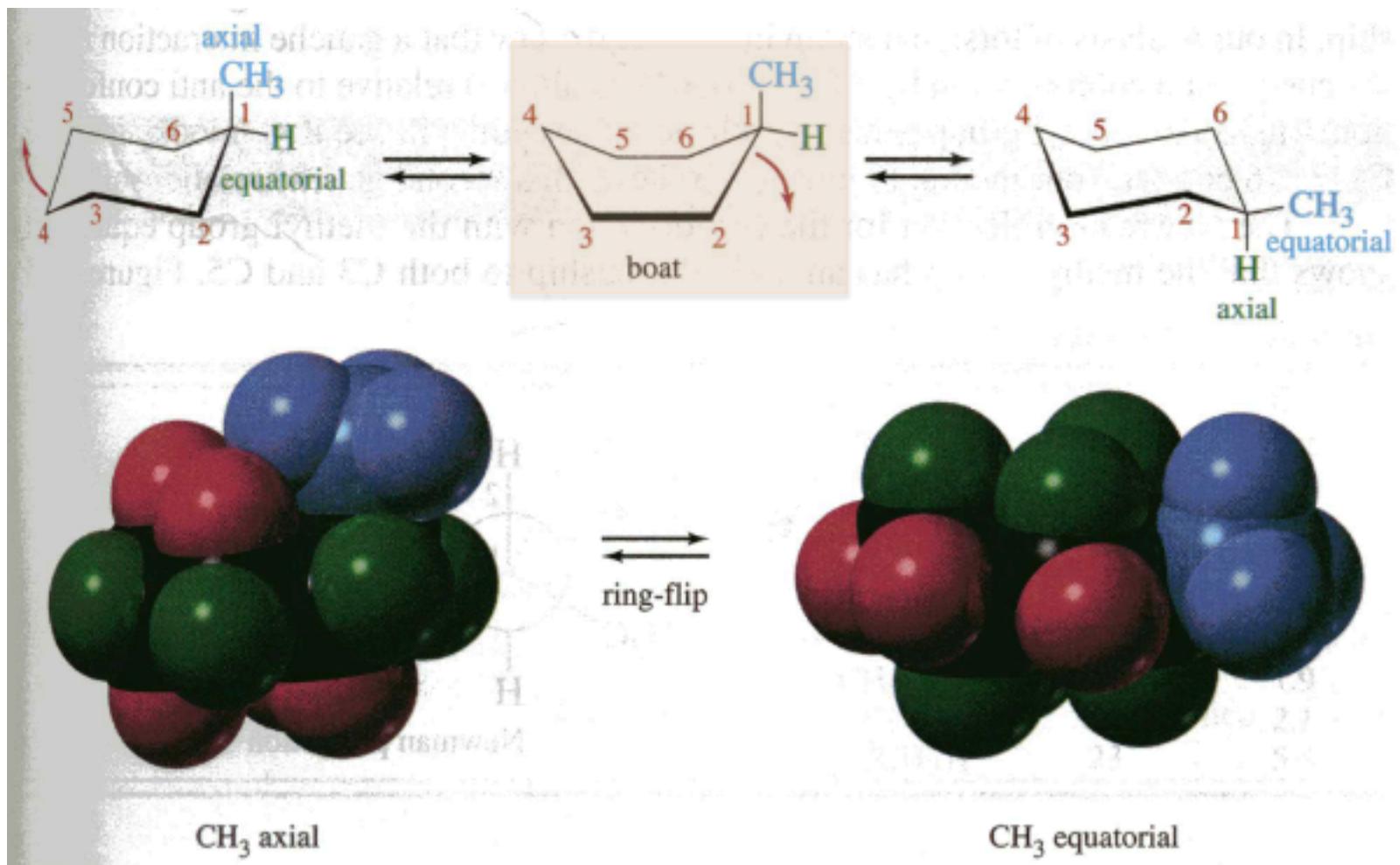
axial and equatorial

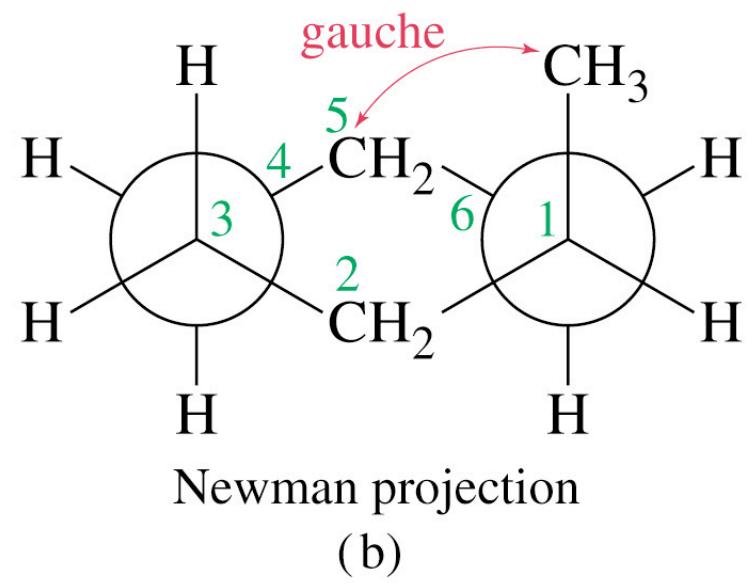
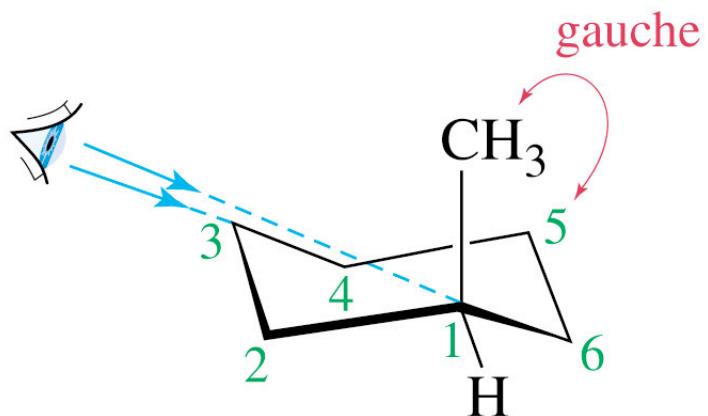
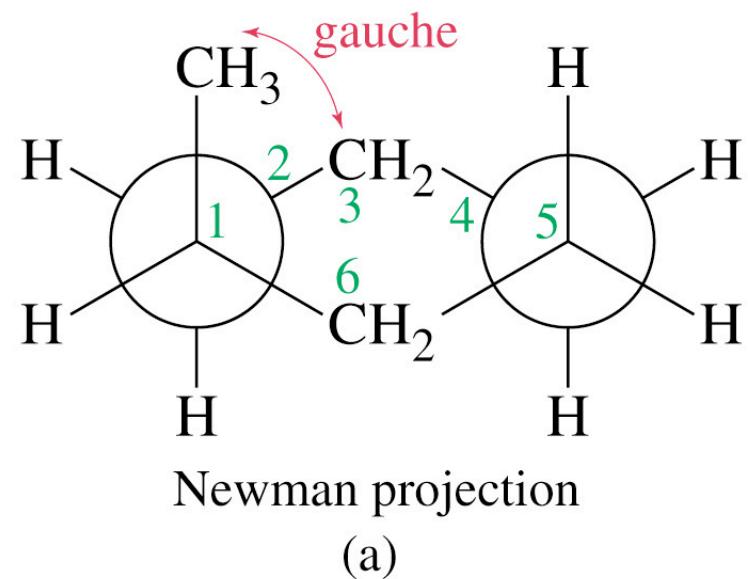
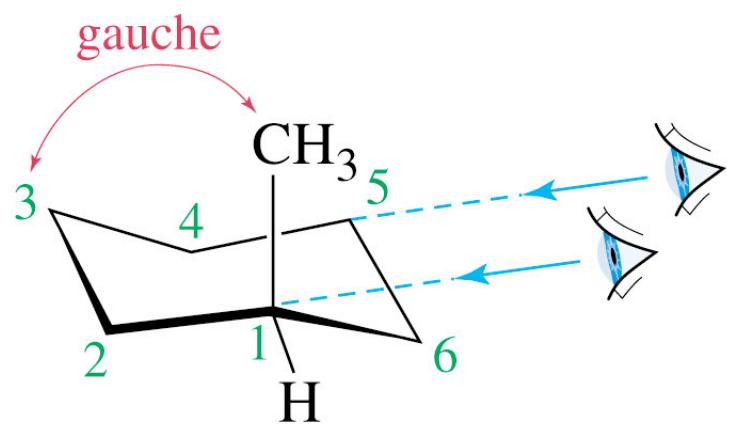


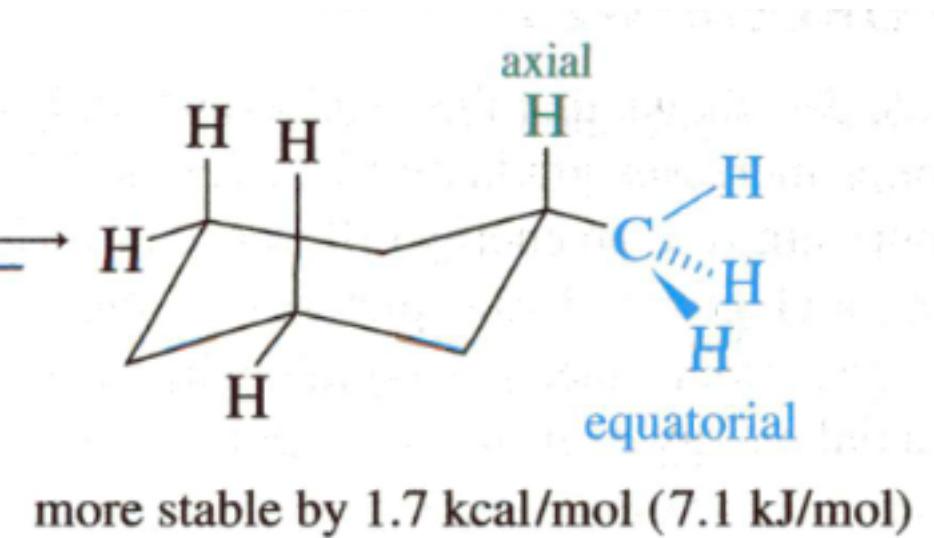
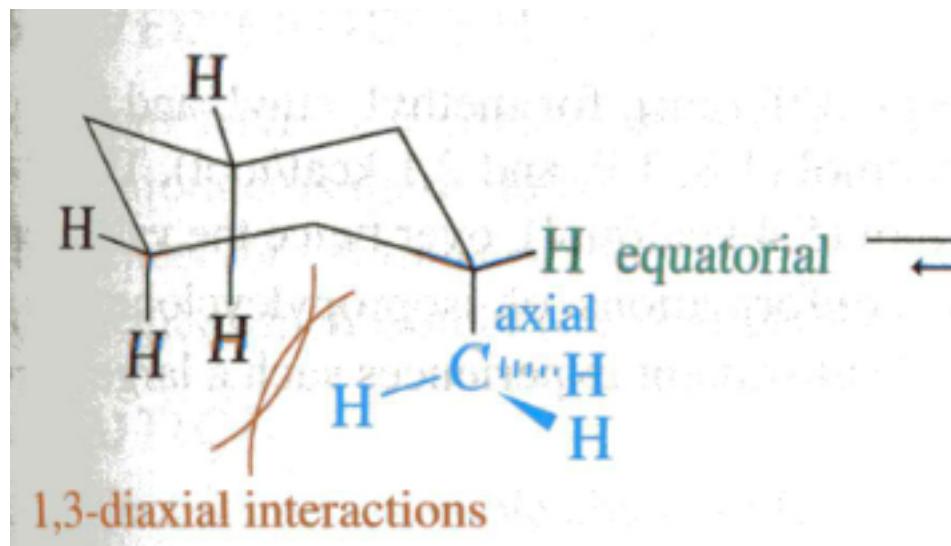
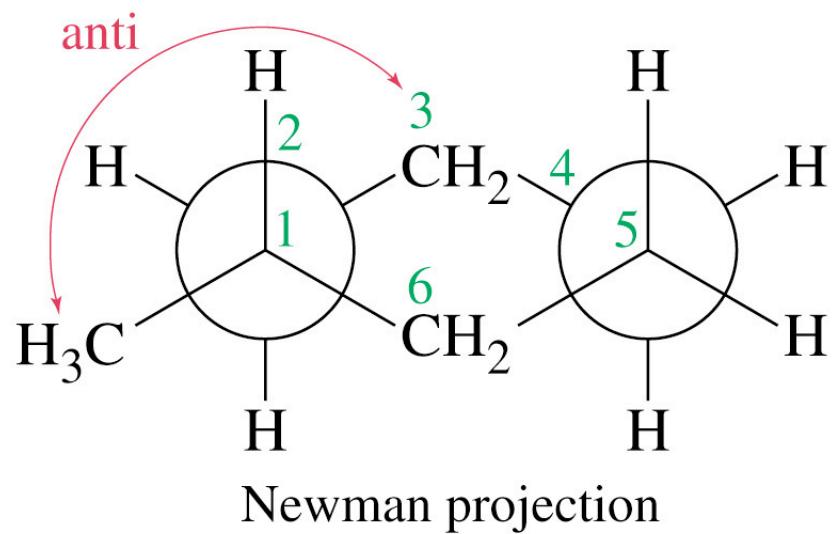
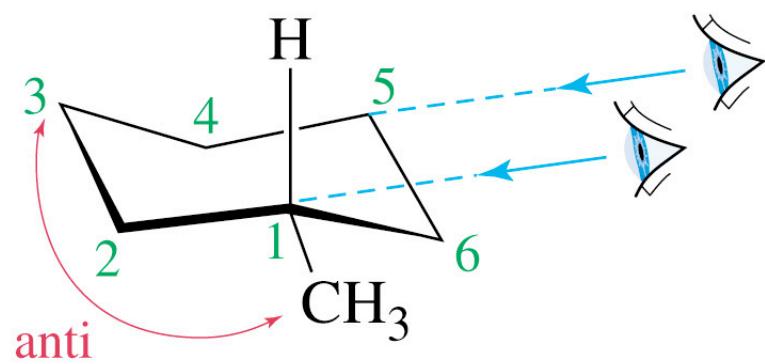
seen from the side

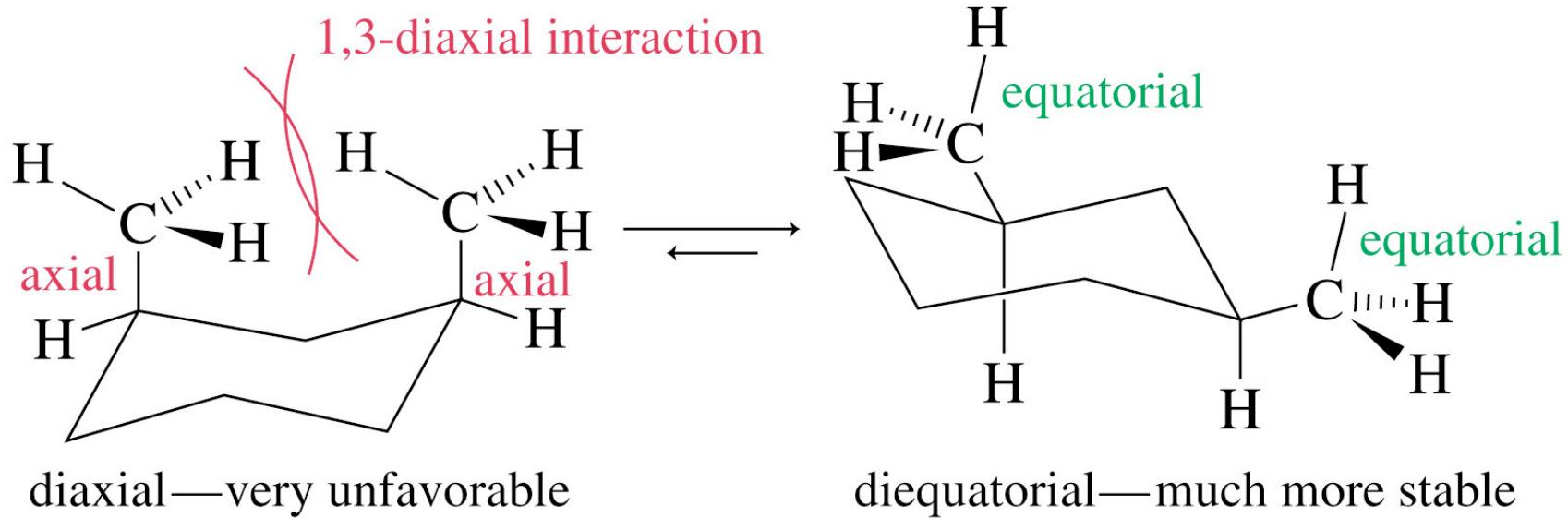


seen from above

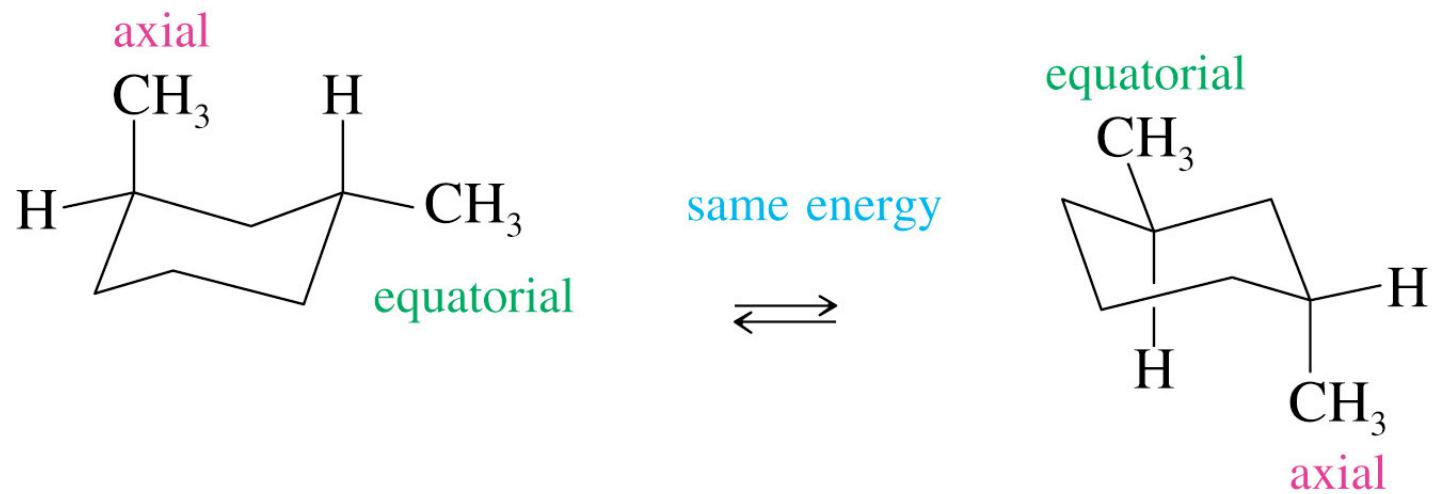




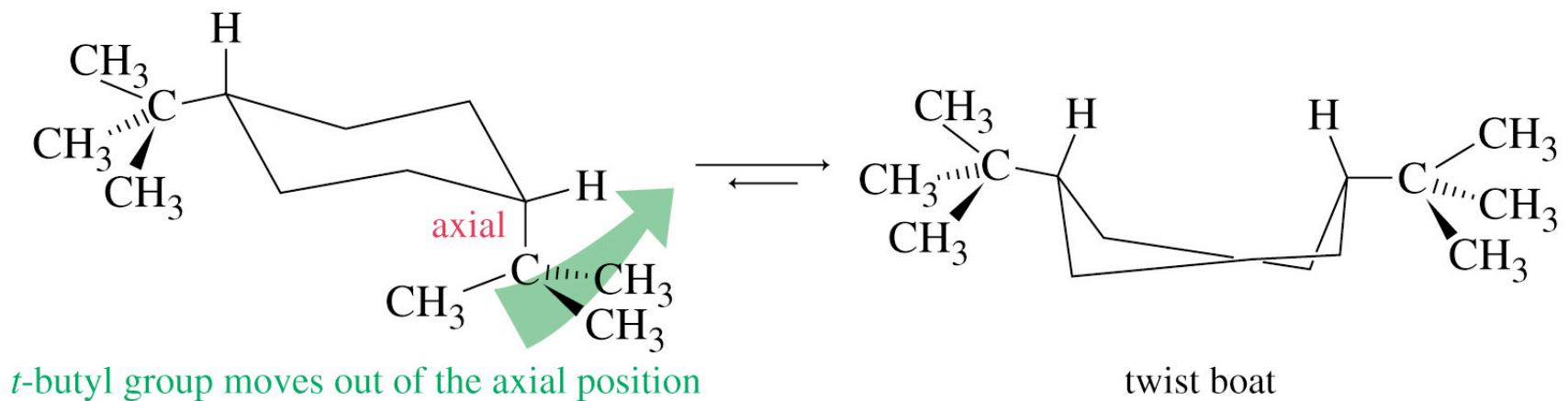
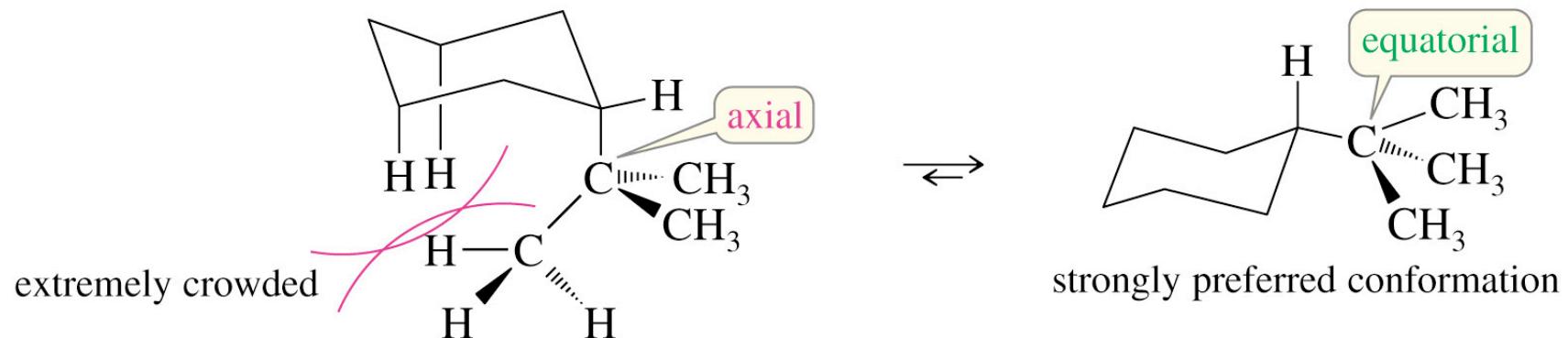




Chair conformations of trans-1,3-dimethylcyclohexane

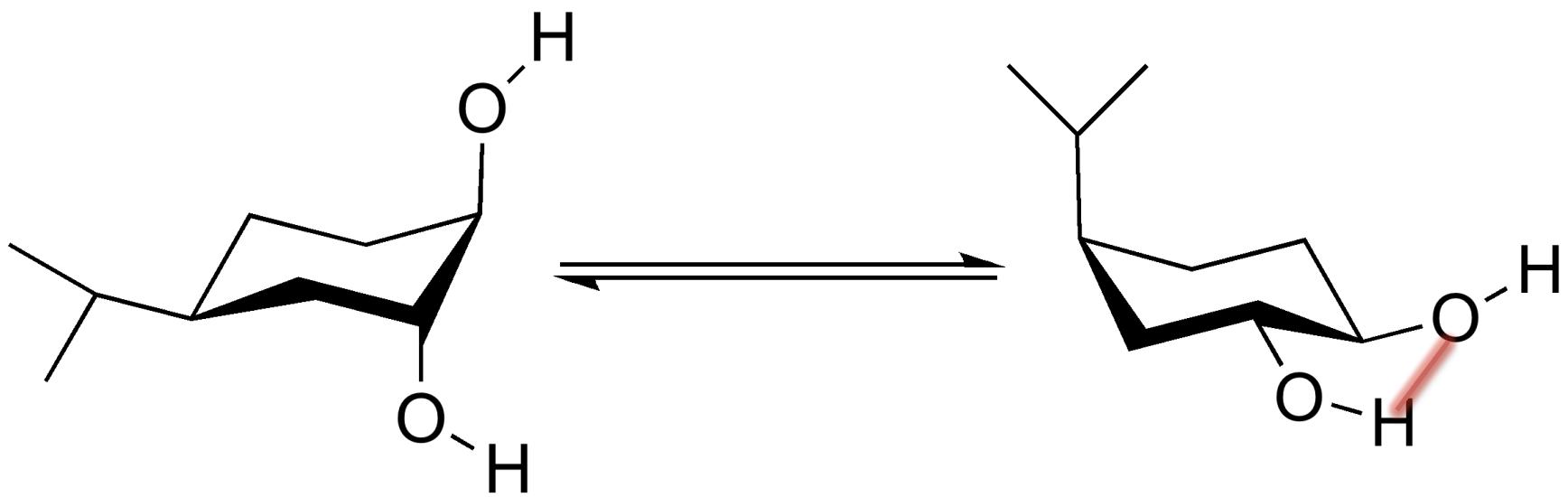


Bulky group



A value ---- the magnitude of the preference (ΔG°) to equatorial

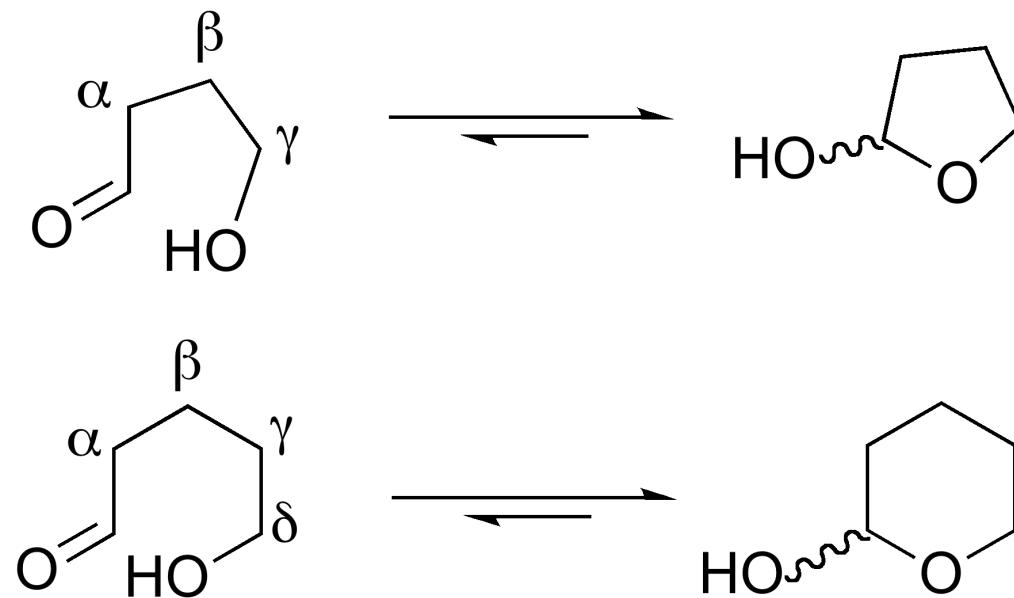
Group	A value	Group	A value	Group	A value
D	0.006	NH ₂	1.23-1.7	C ₆ H ₁₁	2.2
F	0.25-0.42	N(CH ₃) ₂	1.5-2.1	CH ₂ Br	1.79
Cl	0.53-0.64	NO ₂	1.1	Si(CH ₃) ₃	2.5
Br	0.48-0.67	SH	1.21	CH=CH ₂	1.5-1.7
I	0.47-0.61	SO ₂ CH ₃	2.50	CHO	0.56-0.8
OH	0.60-1.04	CH ₃	1.74	COCH ₃	1.0-1.5
OCH ₃	0.55-0.75	C ₂ H ₅	1.79	CO ₂ ⁻	2.0
OC ₆ H ₅	0.65	CH(CH ₃) ₂	2.21	CO ₂ H	1.4
OCOCH ₃	0.68-0.87	CF ₃	2.4-2.5	CO ₂ CH ₃	1.2-1.3
OSi(CH ₃) ₂	0.74	C ₆ H ₅	2.8	CH(CH ₃) ₃	4.7-4.9

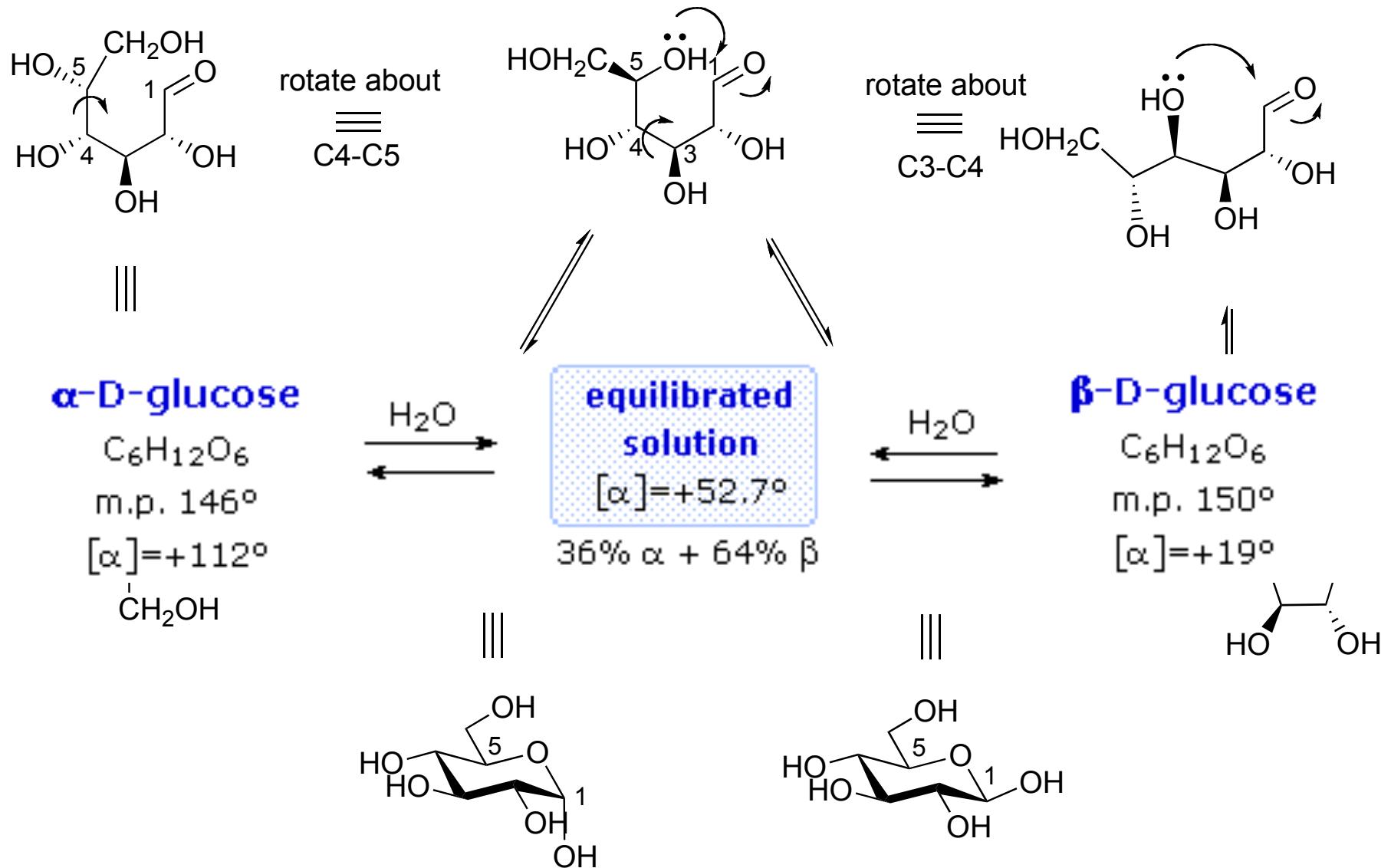


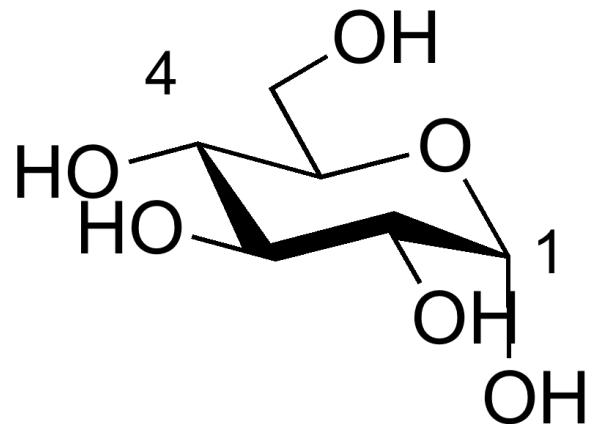
$$\Delta G_{eq}^\circ = A_{ipr} + \boxed{\Delta G_{HB}^\circ} - 2A_{OH}$$

Anslyn, E. V. Modern Physical Organic Chemistry;
JACS, 1994, 116, 2778-2792

2.3 Position of equilibria







4C_1 conformation

lowest

Highest part of chair when viewed from
clockwise numbered face

2.4 Ring structure of other carbohydrates

Pyranose structure is preferred form adopted by hexose

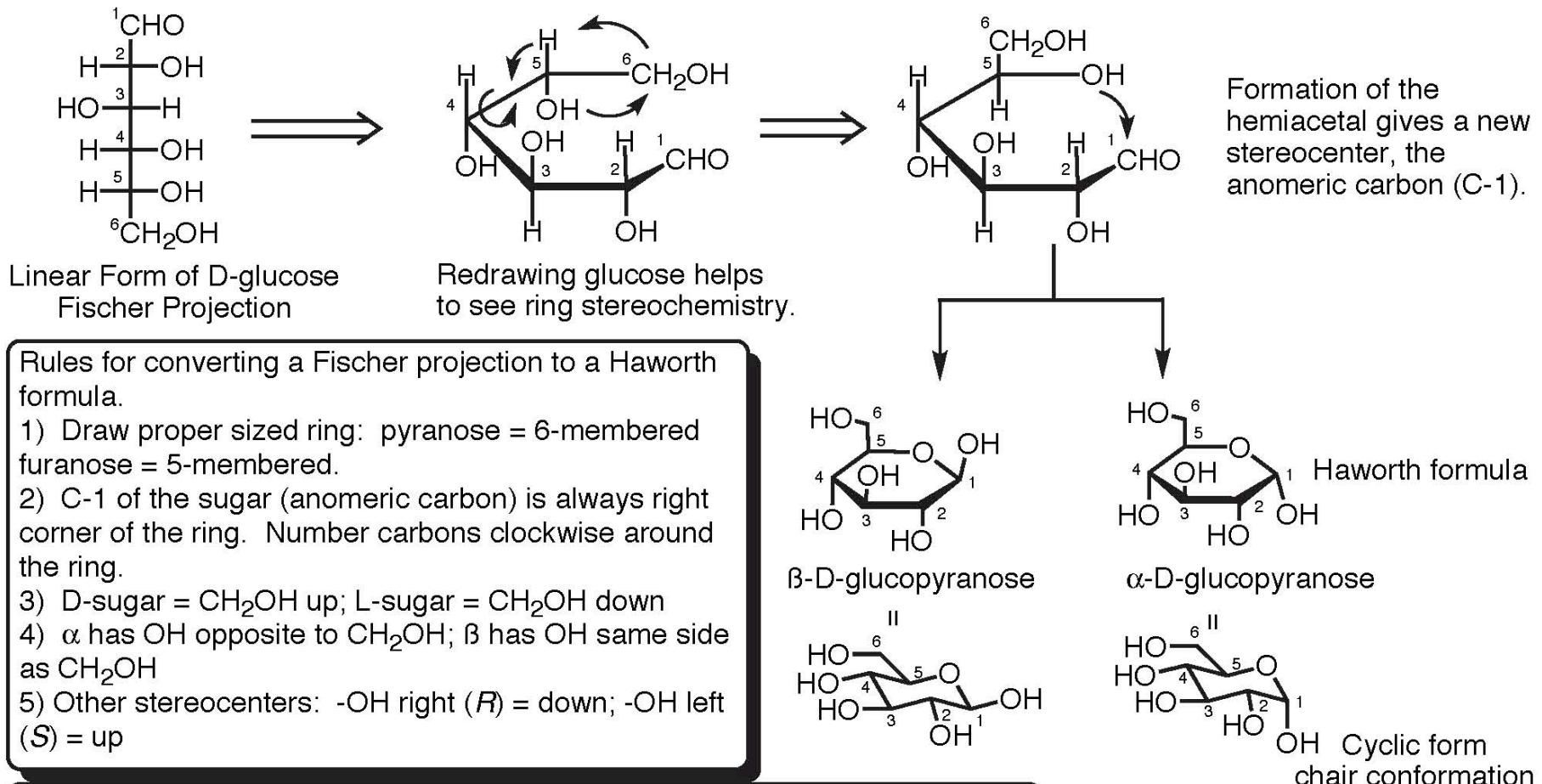
Exist in water as mixtures of α - and β -anomers

Usually in the 4C_1 conformation

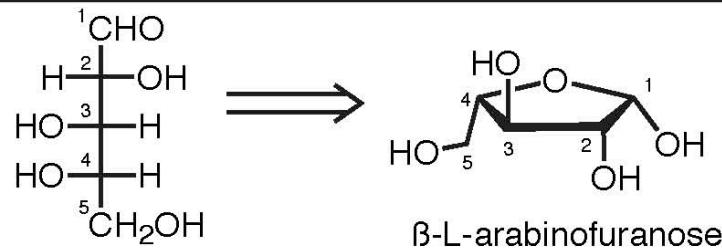
Altrose, idose and talose, which would have several OH in axial positions in this form, have larger amounts of the furanose forms present at equilibrium.

Drawing Haworth Formula

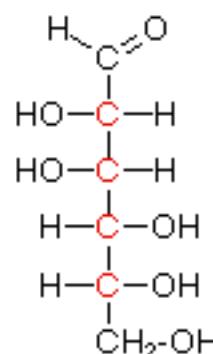
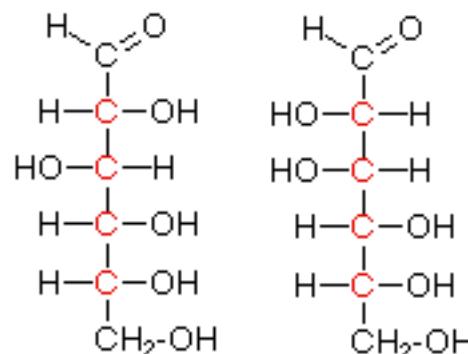
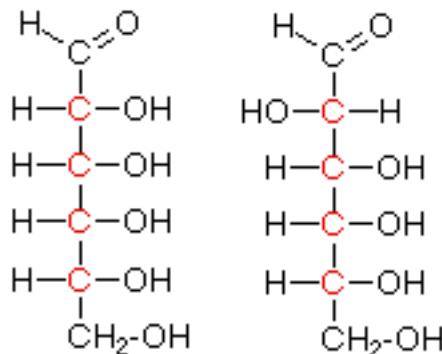
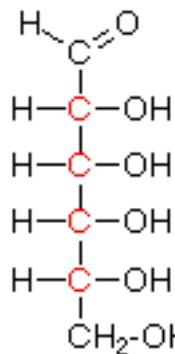
D-Glucose exists primarily as a cyclic hemiacetal



Example - L-arabinose to
 β -furanose form
2 = *R* = down
3 = *S* = up
4 = *S* = L = CH₂OH down



EXERCISES

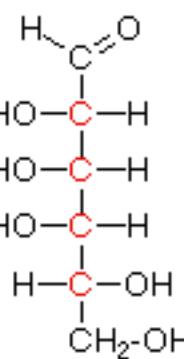
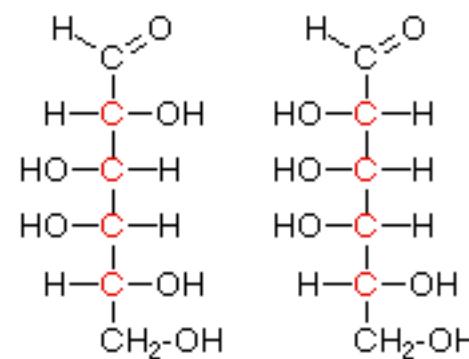
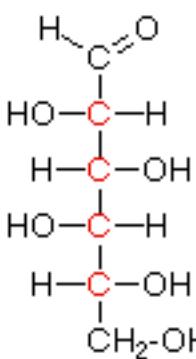
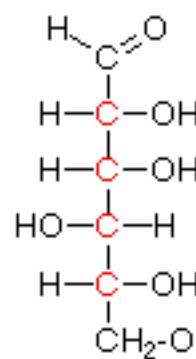


D-(+)-allose

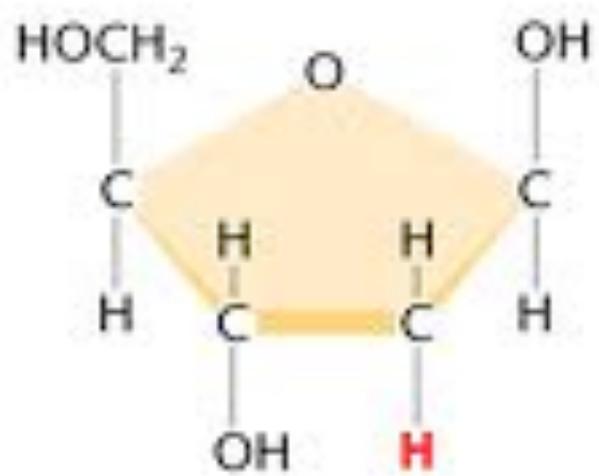
D-(+)-altrose

D-(+)-glucose

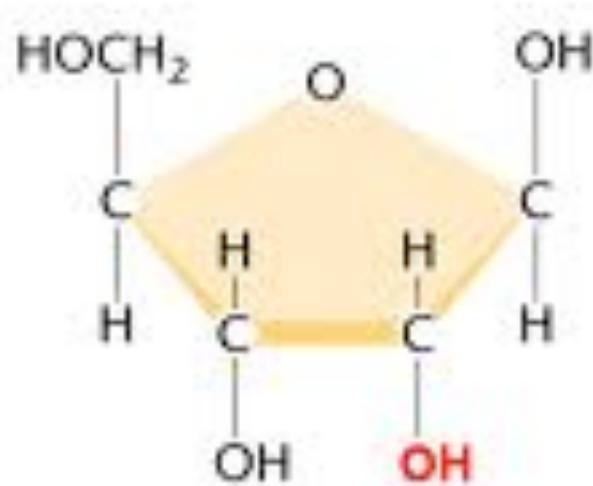
D-(+)-mannose



D-(-)-gulose D-(-)-idose D-(+)-galactose D-(+)-talose



2-Deoxyribose



Ribose

(Hug & Cummings 1997)

The Crystal Structure of D-Ribose—At Last!**

