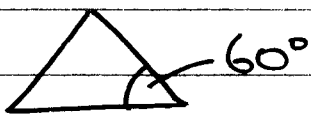
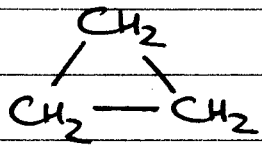


CYCLOALKANES

Problems: 2.10-2.15, 2.31-2.45

Reading: Review Ch2

CYCLOPROPANE

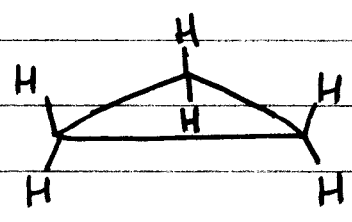


60° very different to 109.5° (TETRAHEDRAL ANGLE)

⇒ ANGLE STRAIN

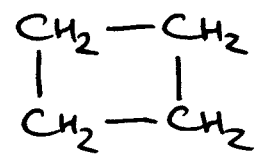
Total ring strain ~ 28 kcal/mol

- most of this is angle strain, but all C-H bonds are eclipsed ⇒ TORSIONAL STRAIN

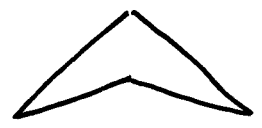


ALL ECLIPSED

- CYCLOBUTANE



IF PLANAR, all C-Hs would be eclipsed, so ring puckers to avoid TORSIONAL STRAIN

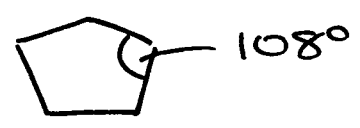


C-C-C angles $\sim 88^\circ$
(so, worse than $90^\circ \Rightarrow$ more ANGLE STRAIN)

Total ring strain is ~ 26 kcal/mol

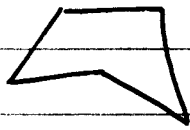
IN ALL CYCLOALKANES LARGER THAN CYCLOPROPANE, NON-PLANAR CONFORMATIONS ARE FAVORED.

- CYCLOPENTANE



IF it were planar,
 $108^\circ \approx 109.5^\circ$
there would be little angle strain

BUT ALL C-H BONDS WOULD BE ECLIPSED
 \Rightarrow TORSIONAL STRAIN



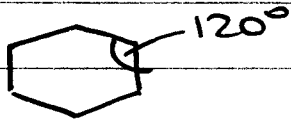
ENVELOPE CONFORMATION (105° ANGLES)

=> REDUCES TORSIONAL STRAIN

4Cs in plane | out (EQUILIBRIUM)

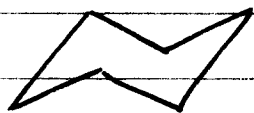
Total ring strain ~ 7 kcal/mol⁻¹

- CYCLOHEXANE



PLANAR STRUCTURE
=> Angle & torsional strain

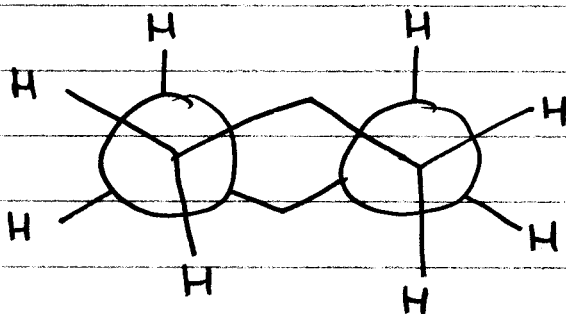
BUT cyclohexane is virtually strain free



CHAIR CONFORMATION
C-C-C ANGLES 109.5°

no angle STRAIN

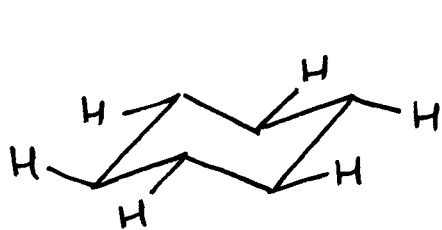
ALSO NO TORSIONAL STRAIN, Hs on ADJACENT CARBON ATOMS STAGGERED



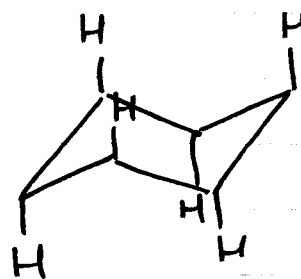
NEWMAN PROJECTION

- ALSO NO STERIC STRAIN

Two Different orientations for C-H BONDS

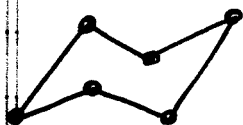


EQUATORIAL



AXIAL

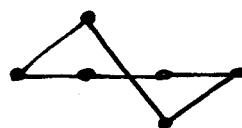
Other cyclohexane conformations



CHAIR



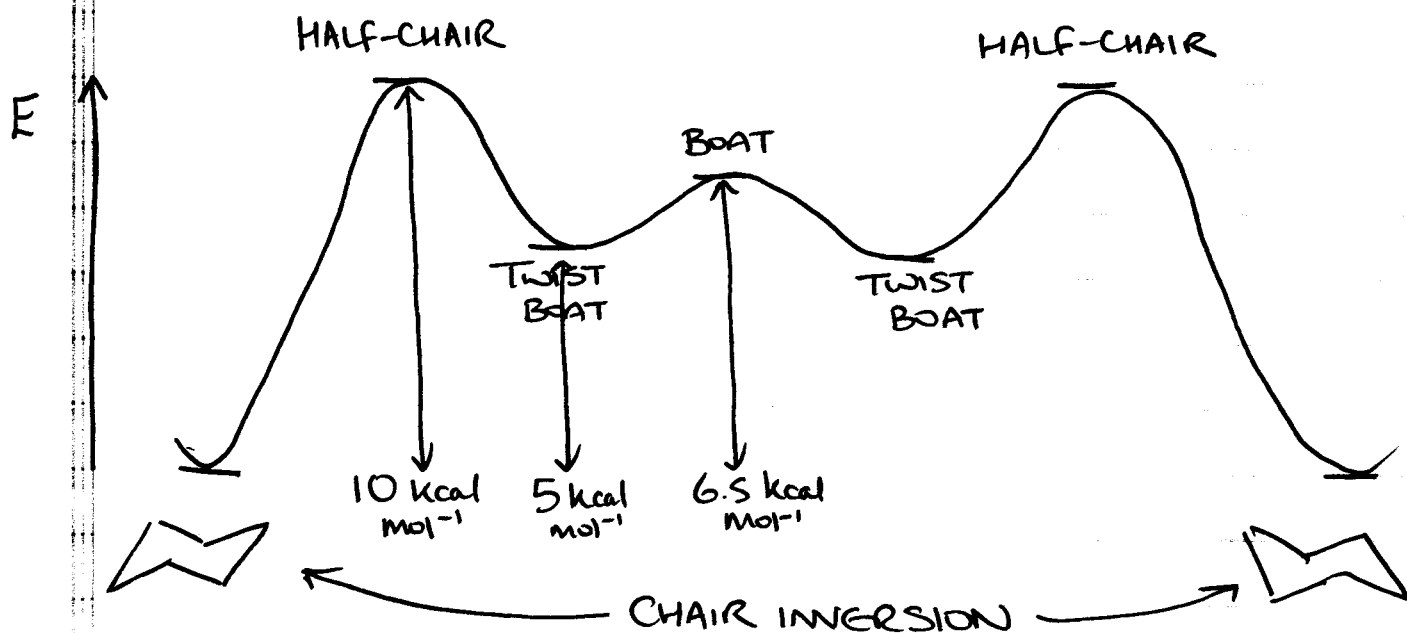
BOAT



HALF-CHAIR

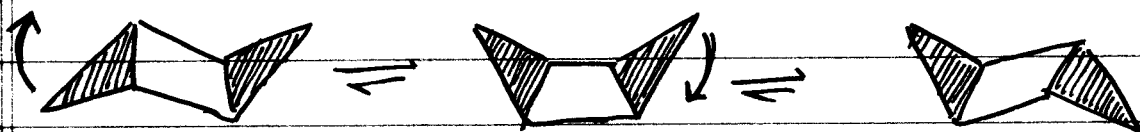


TWIST BOAT

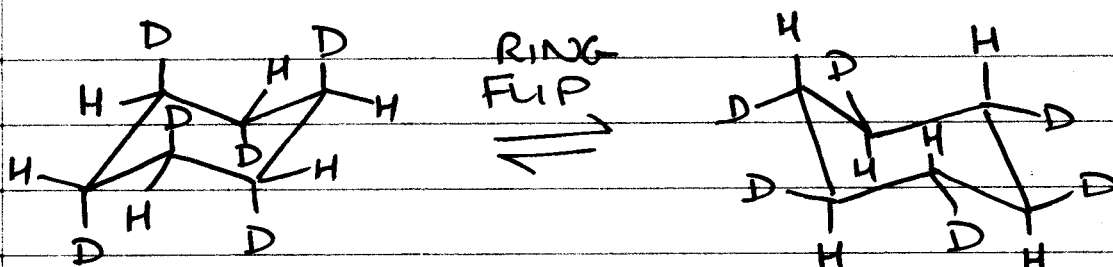


At RT, CHAIR > 99.99% of EQUILIBRIUM MIXTURE

RING-RING FLIP



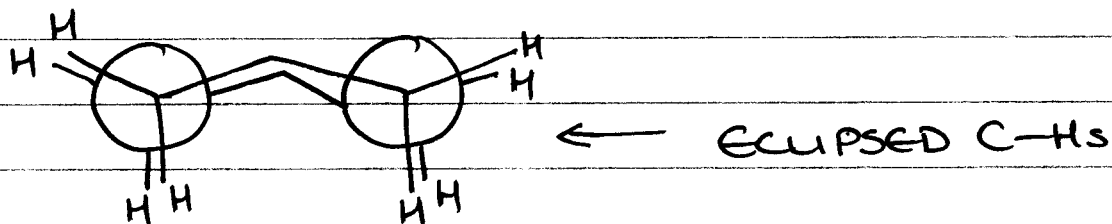
SWITCHES AXIAL & EQUATORIAL POSITIONS



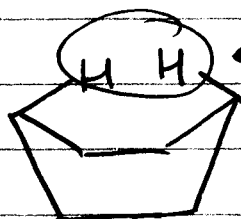
D AXIAL
H EQUATORIAL

D EQUATORIAL
H AXIAL

BOAT CONFORMATION



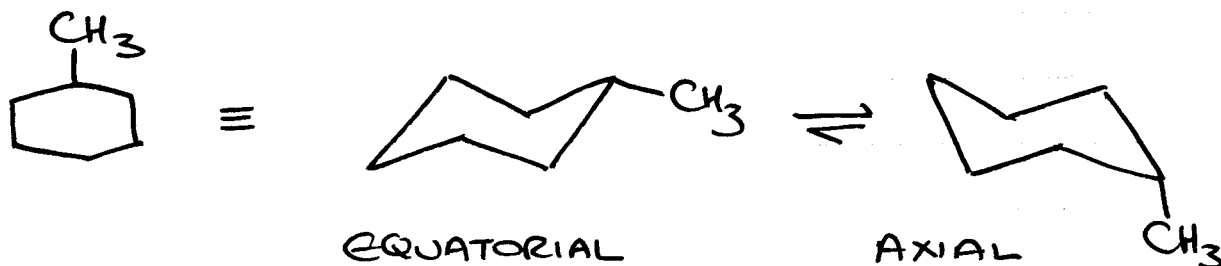
also



NONBONDED
(STERIC)
INTERACTIONS

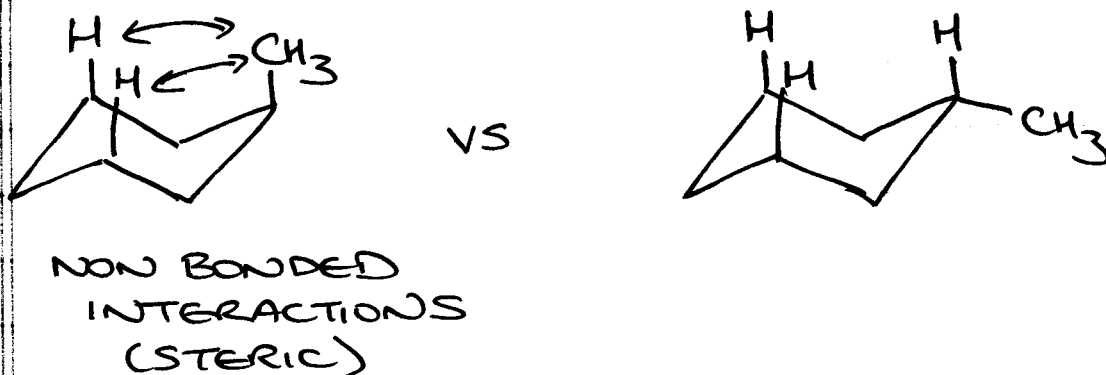
6

Consider METHYL CYCLOHEXANE

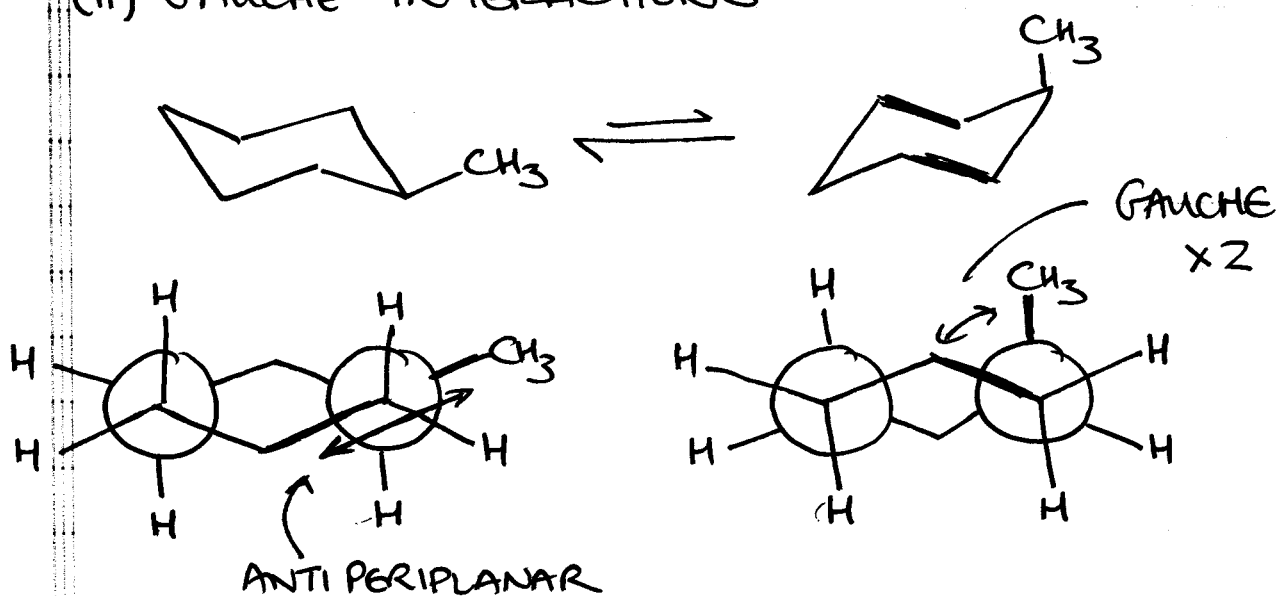


Which is more STABLE?

(i) 1,3 - DIAxIAL INTERACTIONS

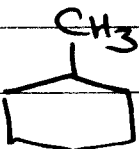


(ii) GAUCHE INTERACTIONS



(7)

In general, conformer in which largest substituent is equatorial will be the most stable

For  equatorial is more stable by ~ 1.74 kcal/mol

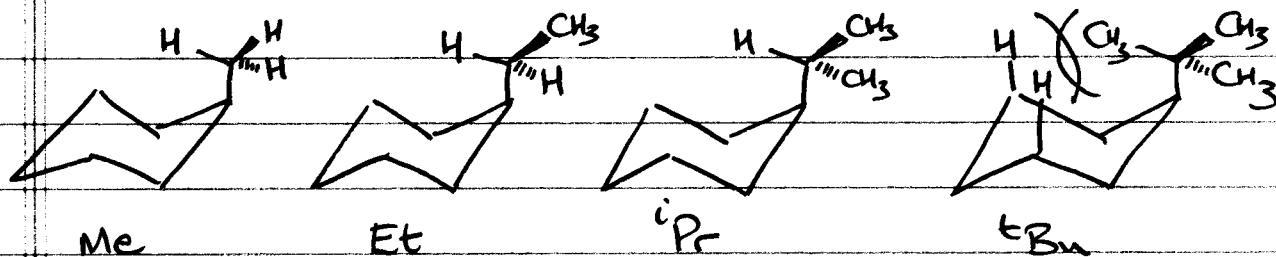
A VALUES \rightarrow measure of preference for the equatorial position

$A = -\Delta G$ change for axial \rightarrow equatorial

So, A values are usually +ve

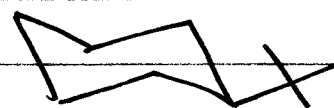
$-\text{CH}_3$	$-\text{CH}_2\text{CH}_3$	$-\text{CH}(\text{CH}_3)_2$	$-\text{C}(\text{CH}_3)_3$
1.74	1.75	2.15	> 5

NOTE small changes for Me, Et, i Pr \leftarrow 1,3-DIAXIAL

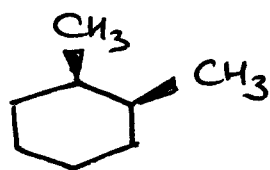


t Bu \Rightarrow LOCKING GROUP \rightarrow

OVERWHELMING PREFERENCE FOR EQUATORIAL POSITION

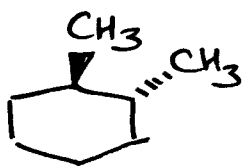


DISUBSTITUTED CYCLOHEXANES



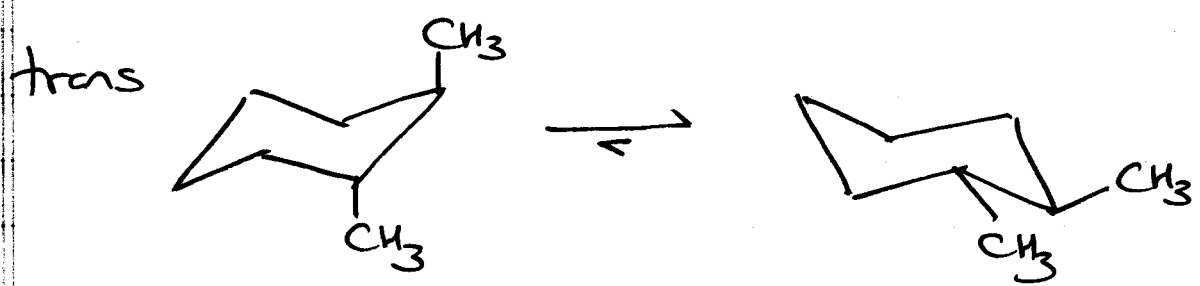
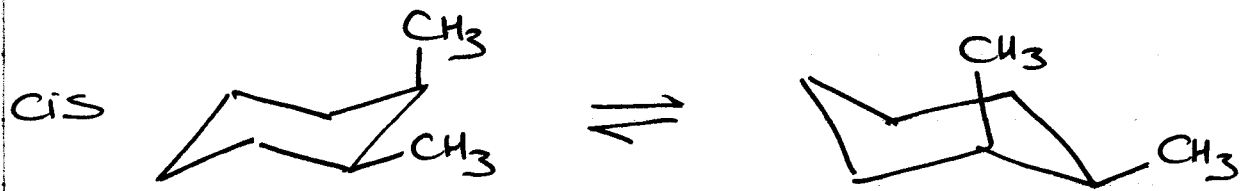
same side cis

cis-1,2-dimethylcyclohexane

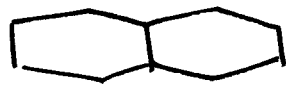


opposite sides trans

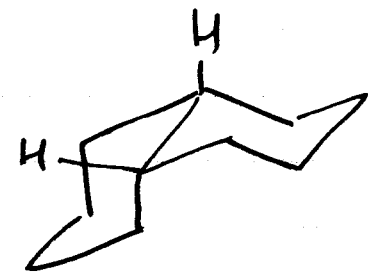
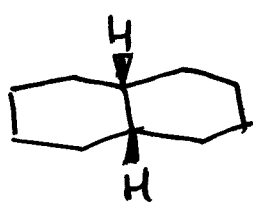
trans-1,2-dimethylcyclohexane



DECALIN



cis decalin



trans decalin

