

①

LEC (8) CHGM 30A

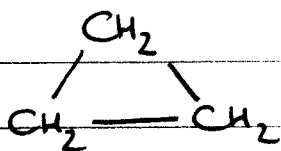
Oct 18th

① CYCLOALKANES

Problems 2.10 - 2.15, 2.31 - 2.45

Reading: Review Ch 2.

CYCLOPROPANE



60° VERY DIFFERENT FROM TETRAHEDRAL ANGLE
109.5°

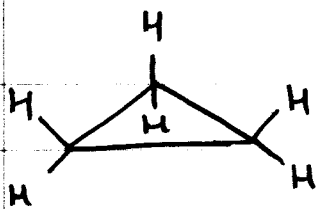
⇒ ANGLE STRAIN

Total ring strain ~ 28 kcal/mol

- most of this is angle strain, but also
all C-H BONDS ARE ECLIPSED

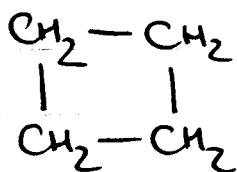
⇒ TORSIONAL STRAIN

(2)



ALL ECLIPSED

- CYCLOBUTANE



If planar, all C-Hs would be eclipsed, so ring puckers to avoid TORSIONAL STRAIN

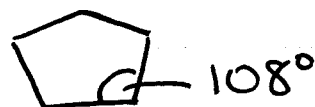
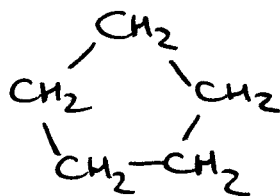


BUT, C-C-C bond angles are now 88°, even worse than 90°, ANGLE STRAIN IS INCREASED

Total ring strain is ~ 26 kcal/mol

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

- CYCLOPENTANE

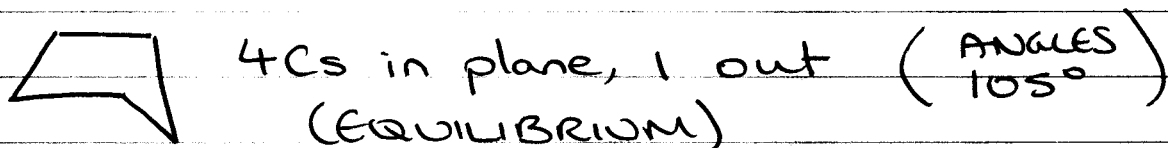


③

If cyclopentane was planar, there would be virtually no angle strain 108 vs 109.5°

BUT again, all C-H bonds would be eclipsed

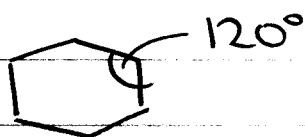
ENVELOPE CONFORMATION



Reduces TORSIONAL STRAIN

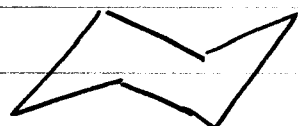
Total ring strain is $\sim 7 \text{ kcal mol}^{-1}$

- CYCLOHEXANE



PLANAR structure would lead to angle strain and torsional strain

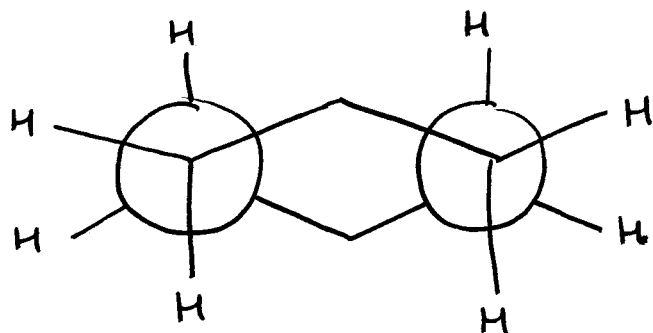
BUT CYCLOHEXANE is virtually STRAIN FREE



CHAIR CONFORMATION

C-C-C ANGLES 109.5°

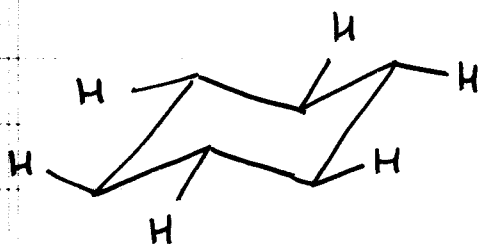
Also, Hs on ADJACENT CARBONS are STAGGERED \Rightarrow NO TORSIONAL STRAIN



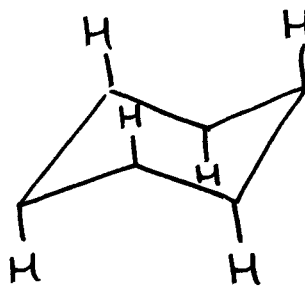
NEWMAN PROJECTION

- ALSO NO STERIC STRAIN (NON BONDED INTERACTION STRAIN)

TWO DIFFERENT ORIENTATIONS FOR C-H BONDS



EQUATORIAL



AXIAL

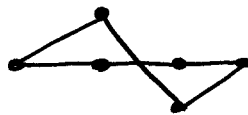
- OTHER CYCLOHEXANE CONFORMATIONS



CHAIR



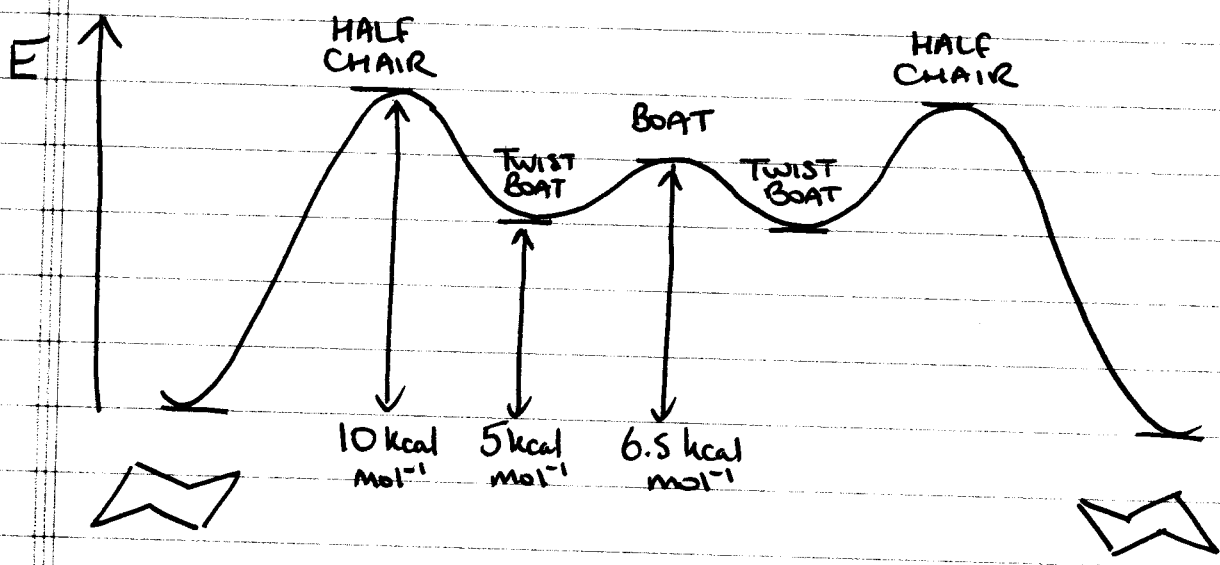
BOAT



HALF-CHAIR

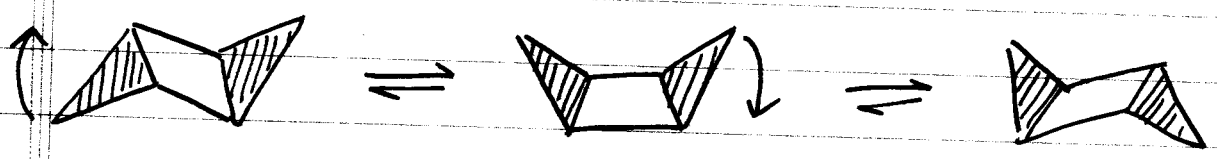


TWIST BOAT

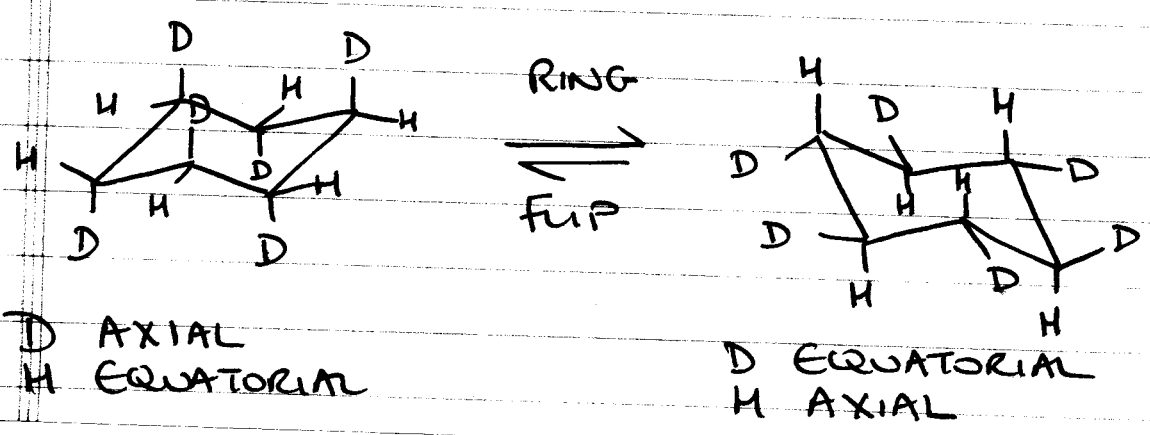


At Room Temp CHAIR > 99.99% of EQUILIBRIUM MIXTURE

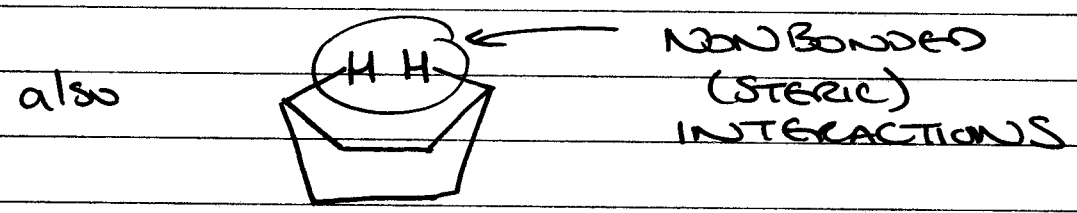
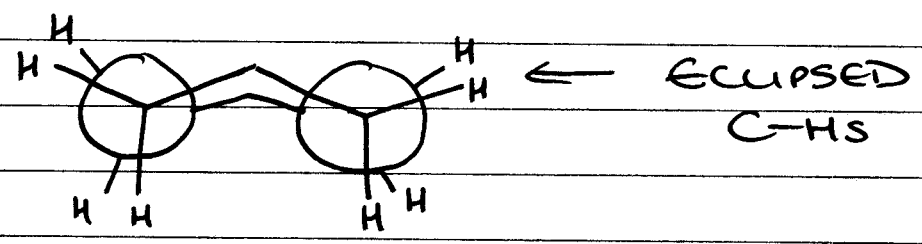
CHAIR INVERSION (RING-RING FLIPPING)



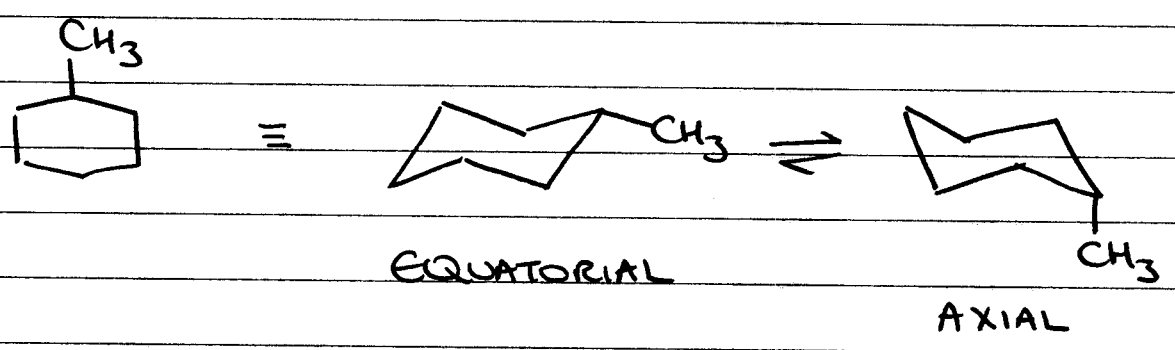
SWITCHES AXIAL & EQUATORIAL POSITIONS



BOAT CONFORMATION

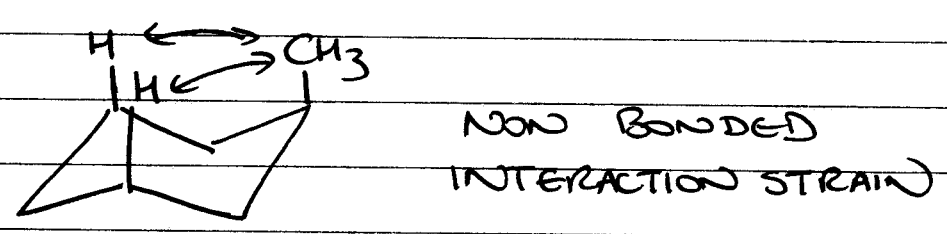


Consider METHYL CYCLOHEXANE

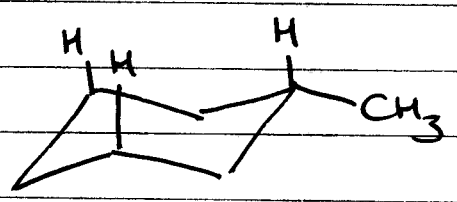


WHICH IS MORE STABLE?

(i) 1,3 DIAxIAL INTERACTIONS

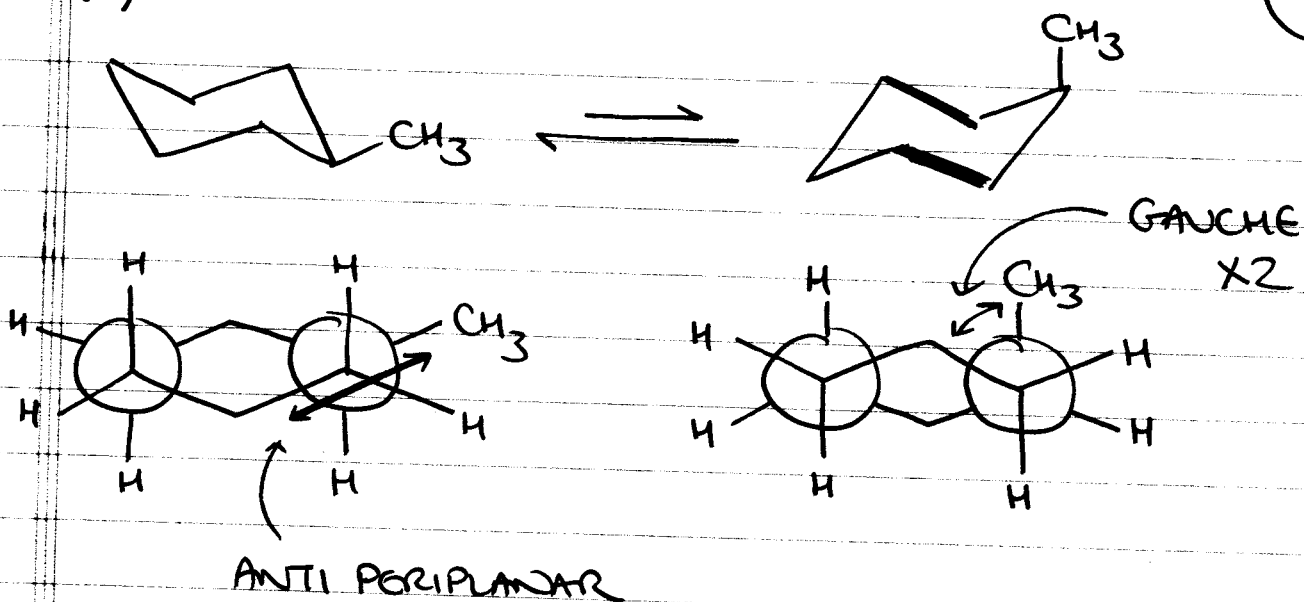


VS

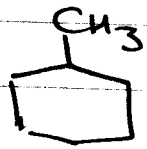


(ii)

7



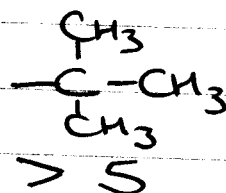
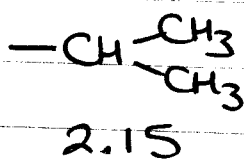
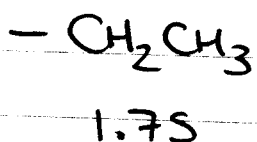
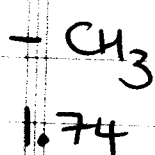
Generally, conformer in which the largest substituent is equatorial will be the most stable

For , equatorial is more stable by $\sim 1.74 \text{ kcal mol}^{-1}$

A values \rightarrow measure of preference for the equatorial position

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

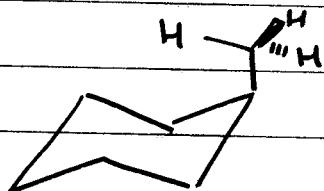
\therefore A values are usually positive



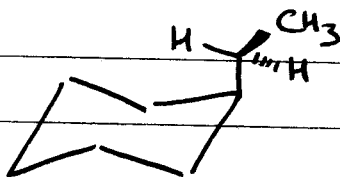
8

Note:

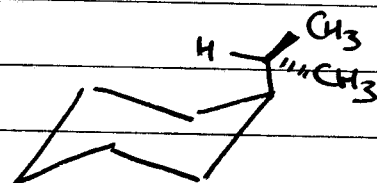
small differences for Me, Et, ⁱPr



Me

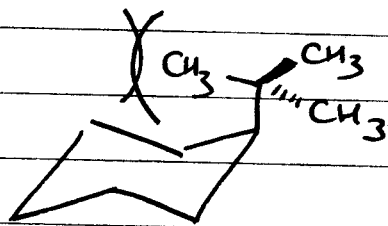


Et

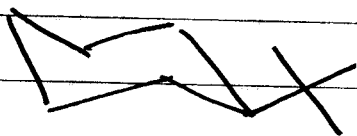


ⁱPr

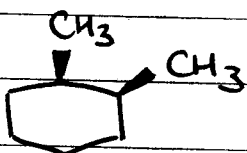
Bu + Bu



+ Bu considered a locking group,
OVERWHELMING PREFERENCE FOR
EQUATORIAL POSITION

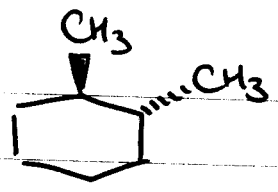


DISUBSTITUTED CYCLOHEXANES

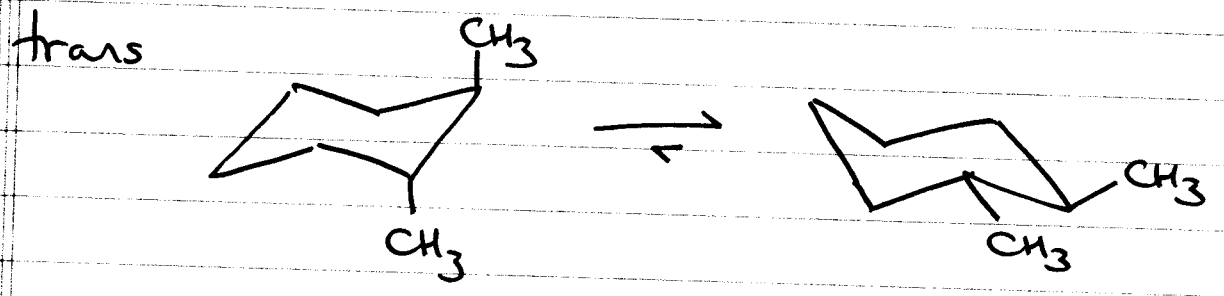
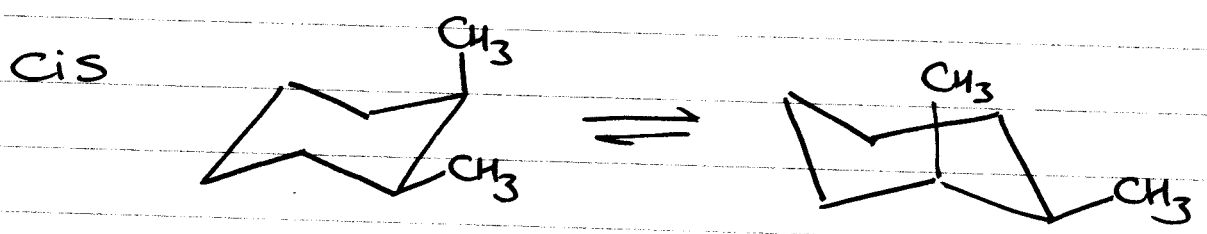


Same side CIS

1,2 DIMETHYLCYCLOHEXANE



opposite sides trans
1,2 DIMETHYLCYCLOHEXANE



— DECALIN

