LEC (7) CHEM 30A Apr 18th

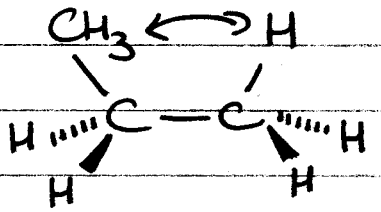
(1) CONFORMATIONAL ANALYSIS
(2) CYCLOALKANES

Read: rest of Ch2
Problems: 2.10-2.12, 2.31-2.33 (3rd)
2.9-2.11, 2.36-2.37 (4th)

---

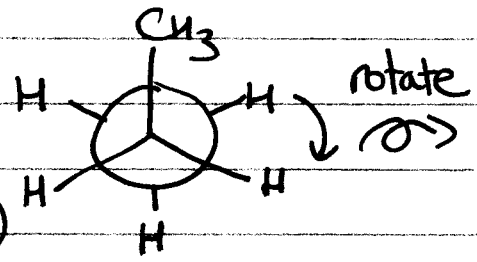
(1) CONFORMATIONAL ANALYSIS

– Propane

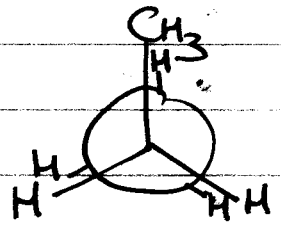


Bigger repulsive interaction
Me–H / C–H

Same profile as ETHANE, but higher barrier (3.4 kcal/mol)

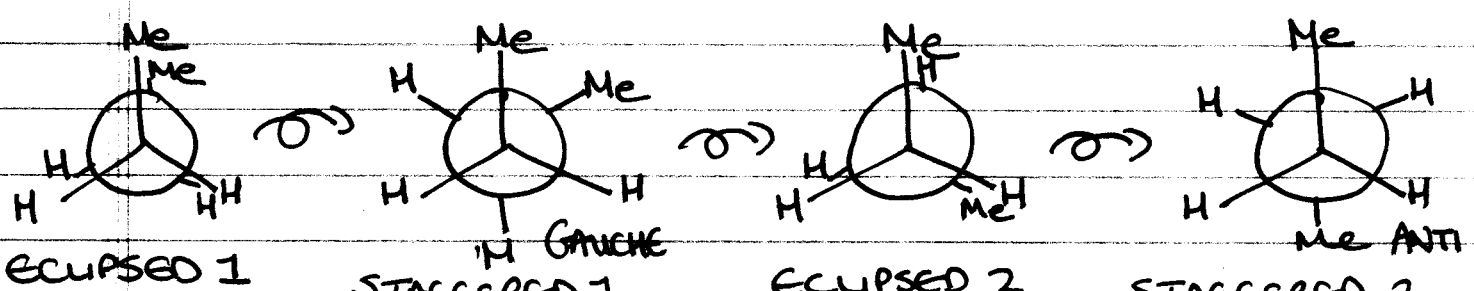


STAGGERED

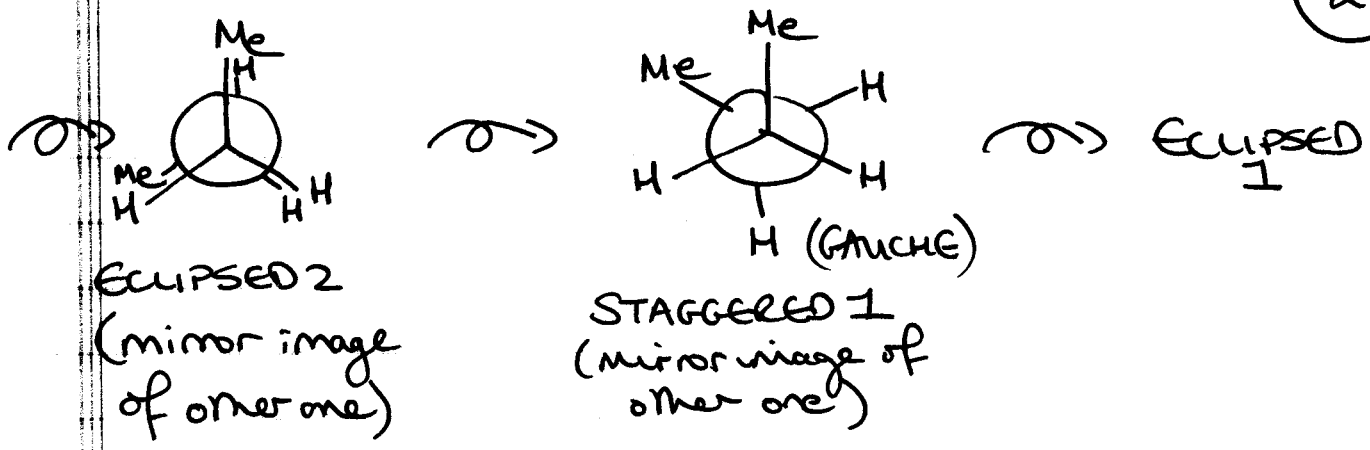


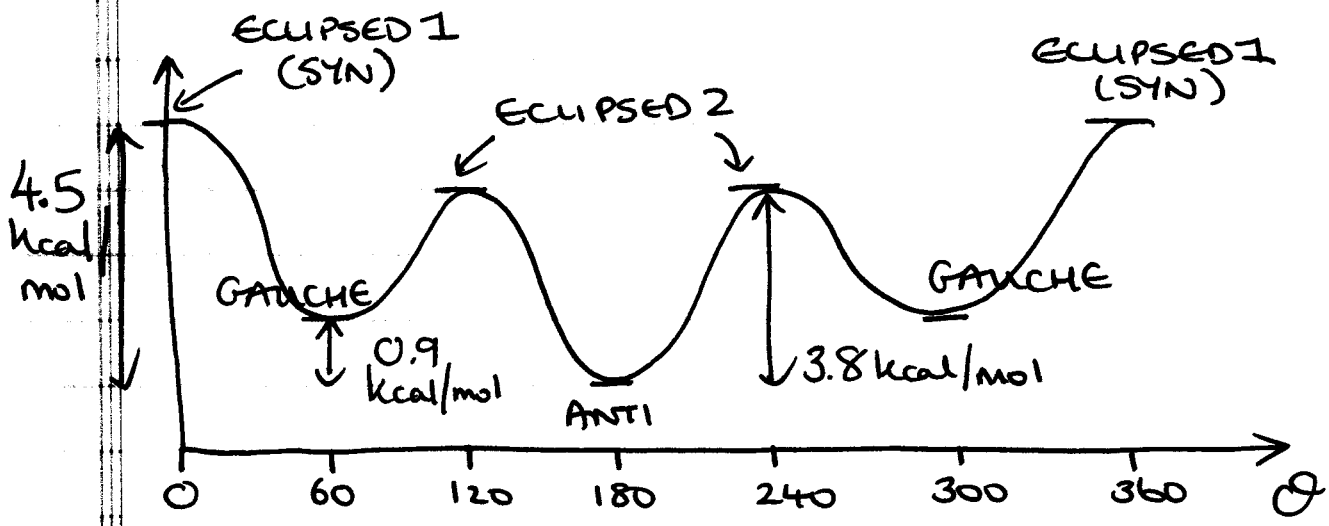
ECLIPSED

– CONFORMATIONS OF BUTANE



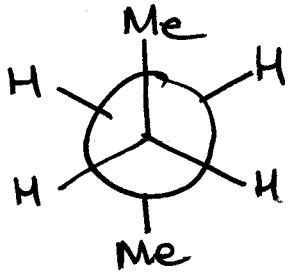
ECLIPSED 1 | STAGGERED 1 (H GAUCHE) | ECLIPSED 2 | STAGGERED 2



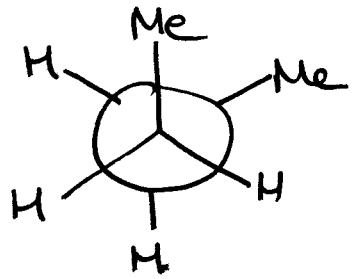


Each ECLIPSED conformer is a MAXIMA
each STAGGERED conformer is a MINIMA

<u>BUT</u> different MINIMA/MAXIMA energies

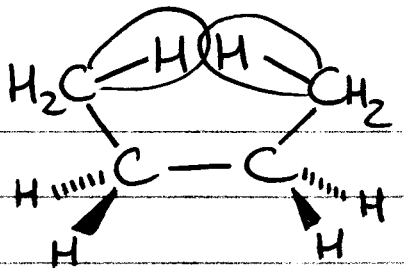


ANTI (180°)



GAUCHE (60°)

Neither is ECLIPSED, but ANTI is more stable than GAUCHE - difference in energy due to STERIC STRAIN



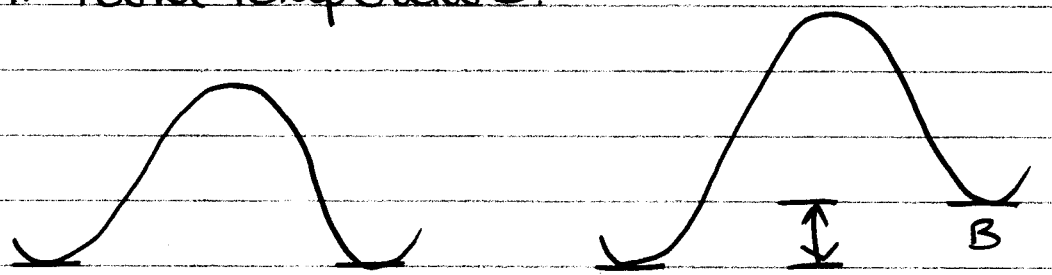
STERIC STRAIN — forcing atoms closer together than atomic radii will allow

At room temperature, BUTANE is rapidly equilibrating between CONFORMERS

~80:20 anti / gauche

Note: very small differences in energy result in very different ratios of conformational isomers.

At room temperature:



K ← equilibrium constant

$A \rightleftharpoons B$

↑ equilibrium arrows

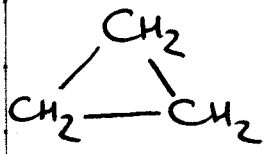
$$K = \frac{[B]}{[A]}$$

$$\Delta G^\circ = -RT \ln K$$

↑ difference in free energy

② CYCLOALKANES

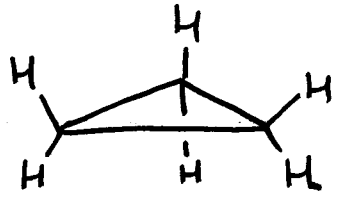
(i) CYCLOPROPANE



60° very different to 109.5° (sp^3 tetrahedral)

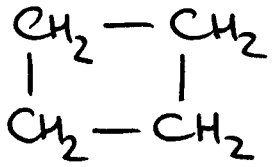
⇒ ANGLE STRAIN

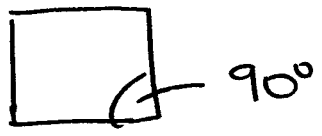
Total ring strain ~ 28 kcal/mol
– most of this is angle strain, but also ALL C–H bonds are ECLIPSED
⇒ TORSIONAL STRAIN



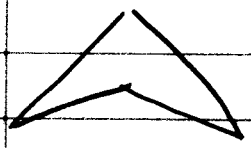
ALL ECLIPSED

(ii) CYCLOBUTANE





If PLANAR, all C–Hs would be eclipsed, so ring puckers to avoid TORSIONAL STRAIN

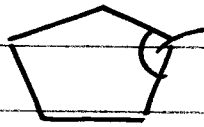


C-C-C angles ~ 88°
(so, worse than 90° => more angle STRAIN)

Total ring strain is ~ 26kcal/mol

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

(iii) CYCLOPENTANE



108° If it were PLANAR 108° ~ 109.5°, there would be little angle strain

BUT all C-H bonds would be ECLIPSED
=> TORSIONAL STRAIN

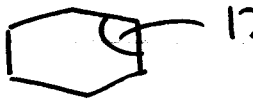
ENVELOPE CONFORMATION (105° ANGLES)

=> REDUCES TORSIONAL STRAIN

4 Cs in PLANE, 1 C OUT (EQUILIBRIUM)

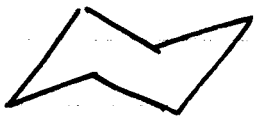
Total ring strain ~ 7 kcal/mol

(iv) CYCLOHEXANE



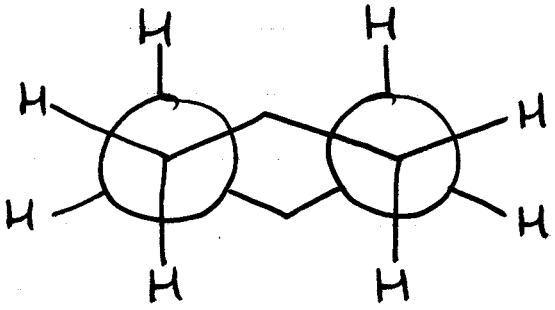
PLANAR STRUCTURE
⇒ angle & torsional strain

But cyclohexane is virtually STRAIN FREE



CHAIR CONFORMATION
C–C–C ANGLES 109.5°
no angle strain

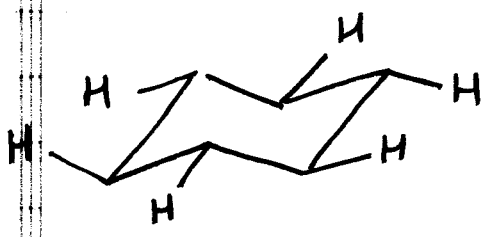
<u>ALSO</u> no torsional strain, Hs on adjacent carbon atoms are staggered.



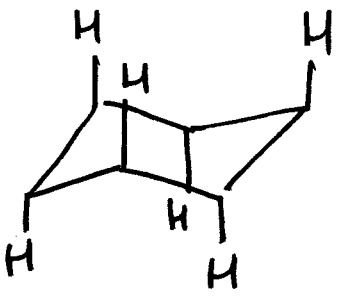
NEWMAN PROJECTION

also, no STERIC STRAIN

TWO DIFFERENT ORIENTATIONS for C–H BONDS

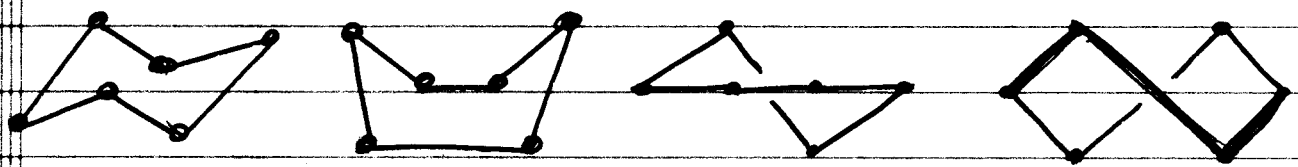


EQUATORIAL

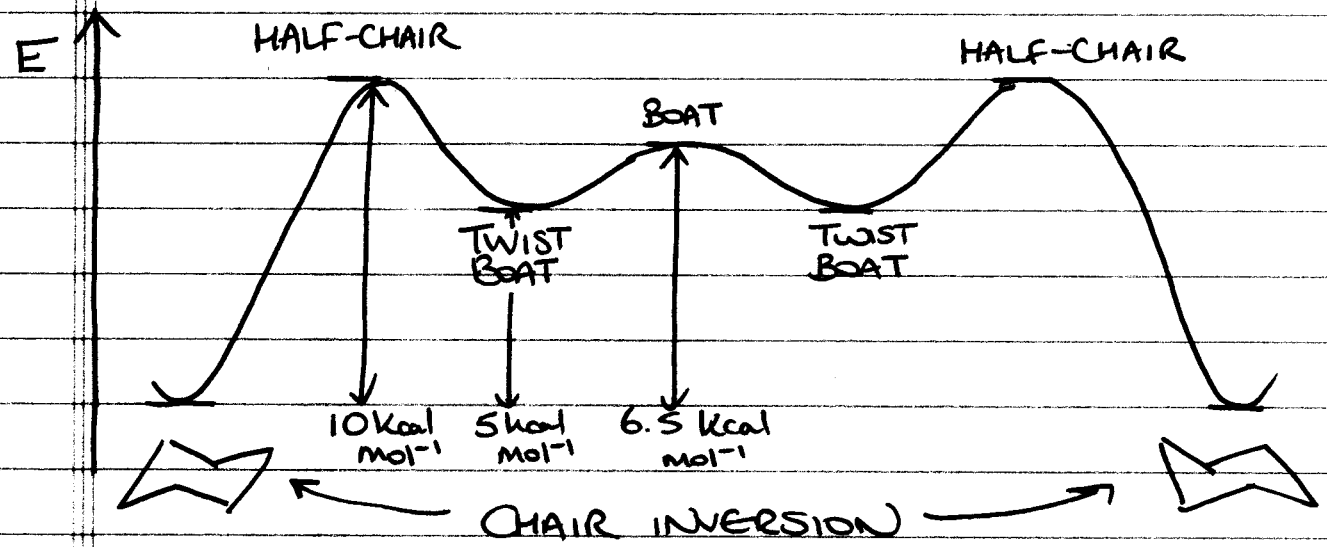


AXIAL

other conformations

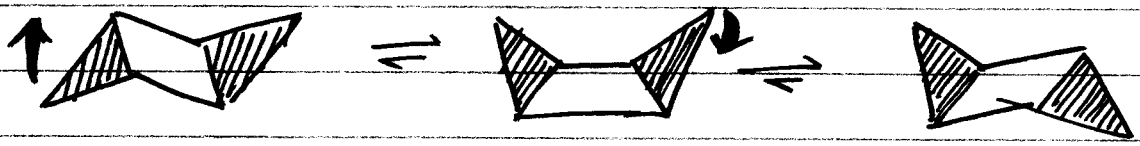


CHAIR BOAT HALF-CHAIR TWIST BOAT



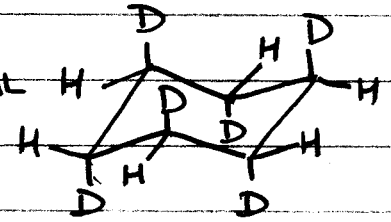
At RT, CHAIR > 99.99% of EQUILIBRIUM MIXTURE

CHAIR FLIP

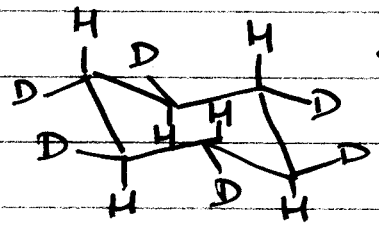


SWITCHES AXIAL & EQUATORIAL POSITIONS

D AXIAL
H EQUATORIAL

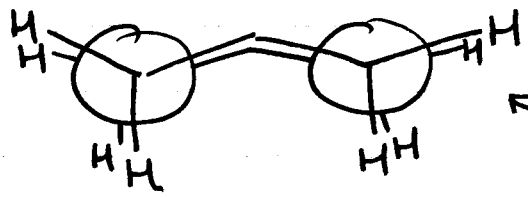


FLIP



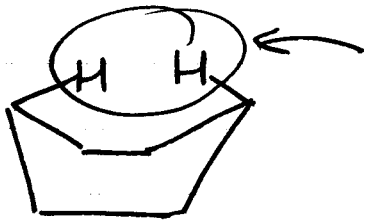
D EQUATORIAL
H AXIAL

BOAT CONFORMATION



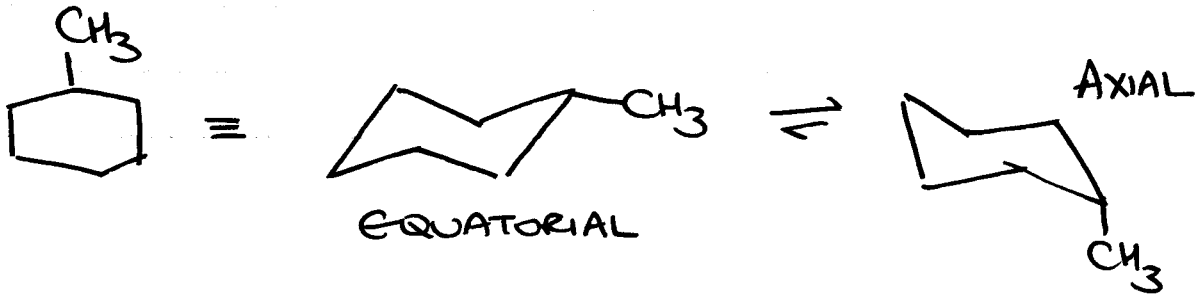
← ECLIPSED C–Hs

also



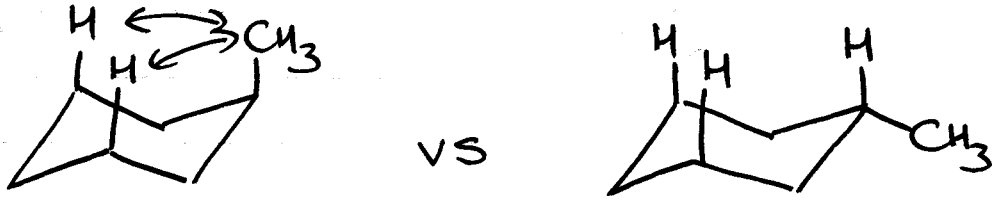
← NONBONDED – STERIC INTERACTIONS

consider METHYL CYCLOHEXANE



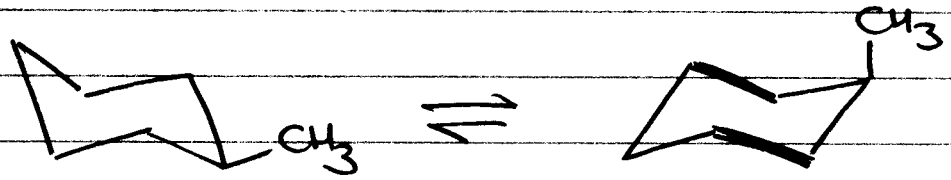
Which is more STABLE?

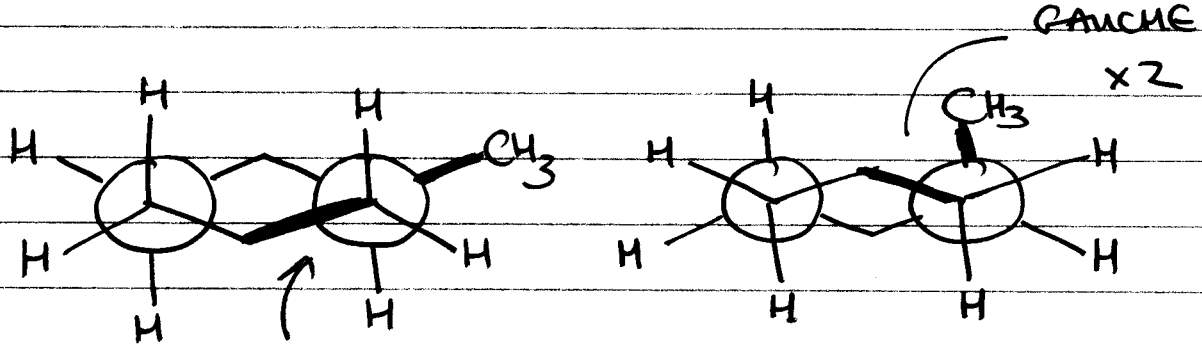
(i) 1,3 – DIAXIAL INTERACTIONS



NONBONDED INTERACTIONS (STERIC)

(ii) GAUCHE INTERACTIONS





ANTI PERIPLANAR