

1 CONFORMATIONAL ANALYSIS

2 CYCLOALKANES

Read: rest of Ch2 Problems 2.9-2.11, 2.36, 2.37

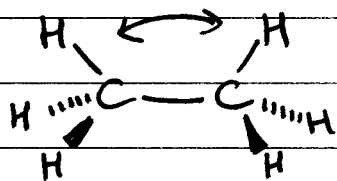
Quiz low 0, high 36, mean 14

1 CONFORMATIONAL ANALYSIS

TORSIONAL STRAIN

- ETHANE, why is there a barrier to rotation

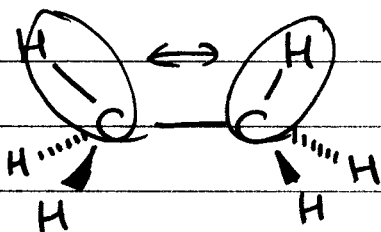
(i) STERIC INTERACTION? (steric => forcing atoms closer than atomic radii allow)



BUT H, very small

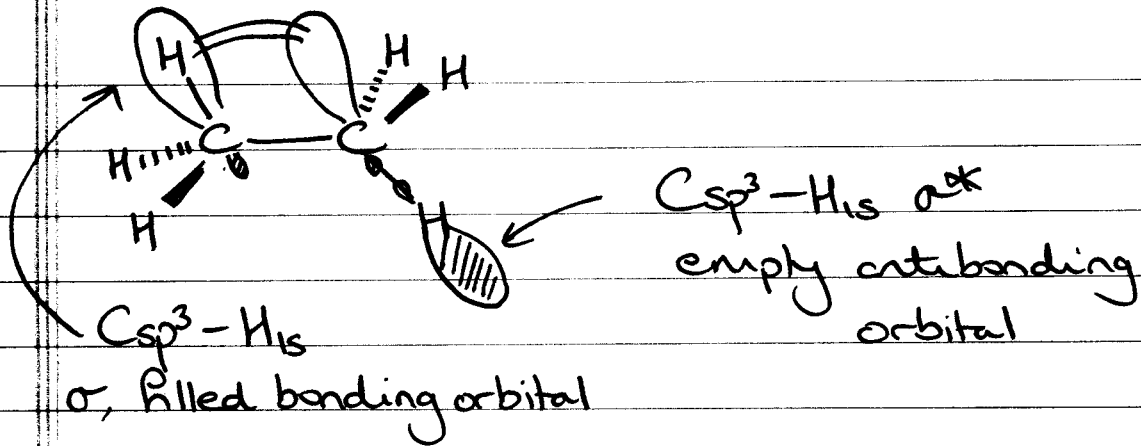
sterics account for ~10% of BARRIER

(ii) ELECTRON PAIR REPULSION

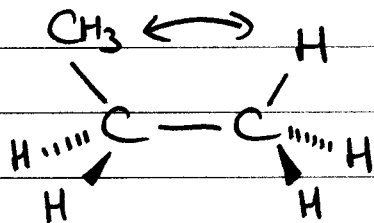


BIGGEST FACTOR

(iii) ATTRACTIVE INTERACTION

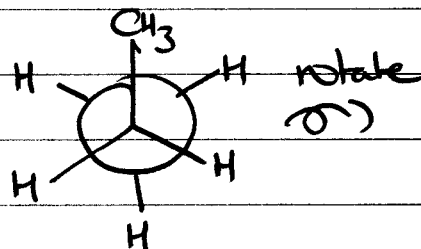


PROPANE

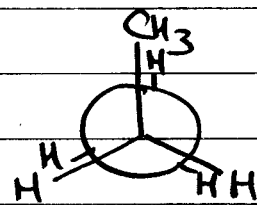


Bigger repulsive interaction
max C-H/C-H

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

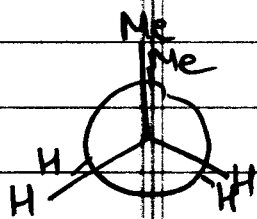


STAGGERED



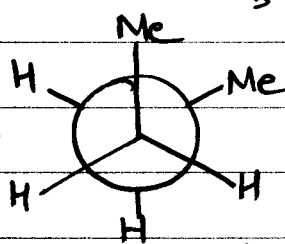
ECLIPSED

BUTANE



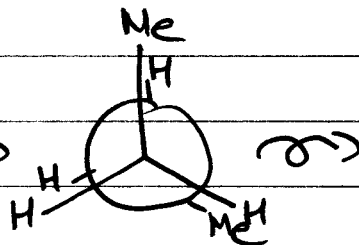
ECLIPSED 1
(SYN)

σ



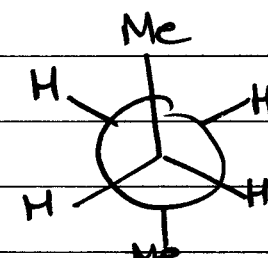
STAGGERED 1
(GAUCHE)

σ



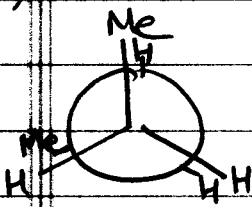
ECLIPSED 2

σ



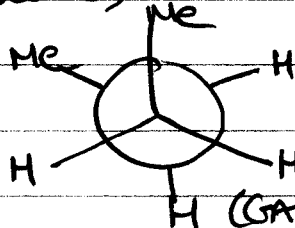
STAGGERED 2
(ANTI)

σ



ECLIPSED 2
(MIRROR IMAGE)

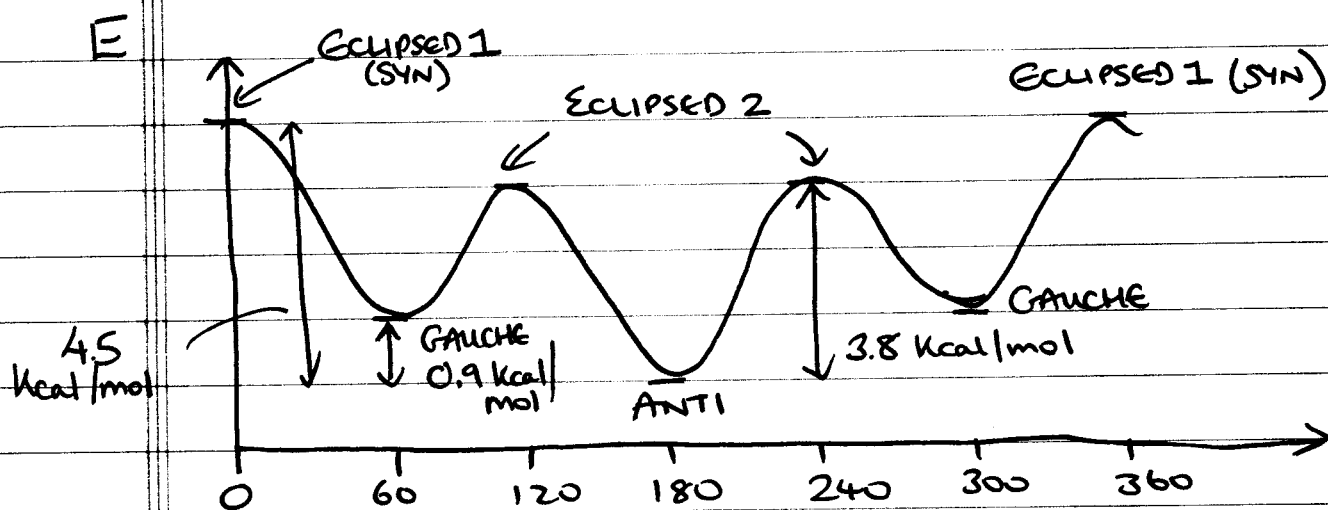
σ



STAGGERED 1
(MIRROR IMAGE)

σ

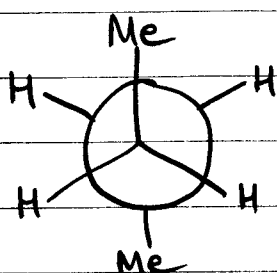
ECLIPSED 1



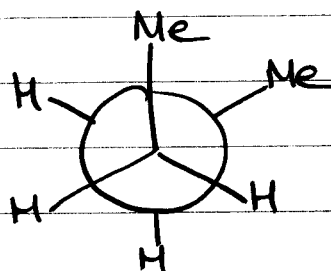
EACH ECLIPSED CONFORMER → MAXIMA

EACH STAGGERED CONFORMER → MINIMA

BUT DIFFERENT MAXIMA/MINIMA ENERGIES

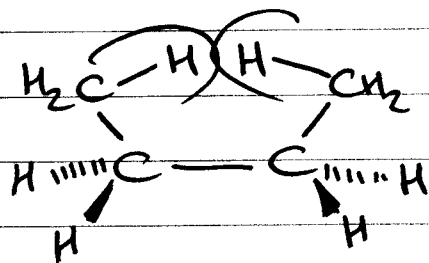


ANTI
(180°)



GAUCHE
(60°)

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

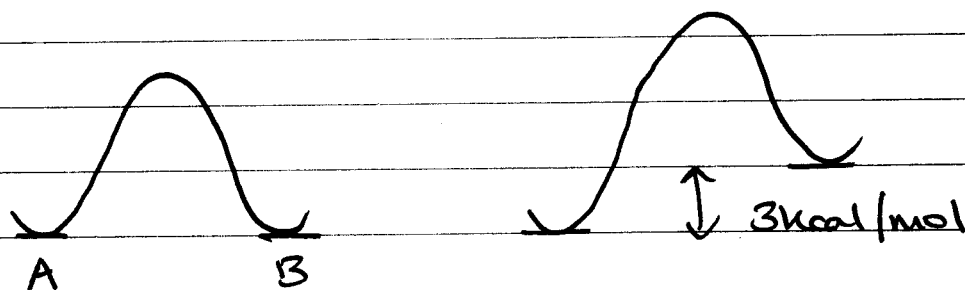


← STERIC STRAIN - forcing atoms closer together than atomic radii will allow.

AT RT, butane is an 80:20 MIXTURE (anti/gauche) of rapidly equilibrating conformers

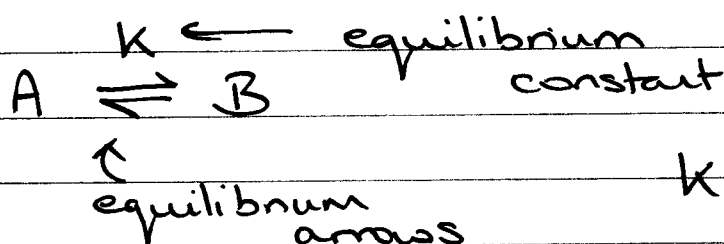
Note: very small differences in energy result in very different ratios of conformational isomers.

At room temperature:



50:50

99:1



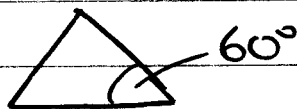
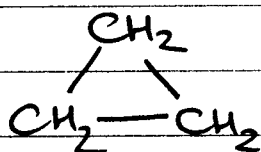
$$K = \frac{[B]}{[A]}$$

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

↖ difference in free energy

② CYCLOALKANES

(i) CYCLOPROPANE



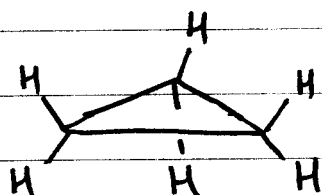
60° very different to 109.5° (sp³ tetrahedral)

⇒ ANGLE STRAIN

5

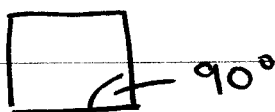
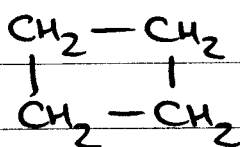
Total ring strain $\sim 28 \text{ kcal/mol}$

- most of this is angle strain, but also
All C-H bonds are eclipsed
 \Rightarrow TORSIONAL STRAIN

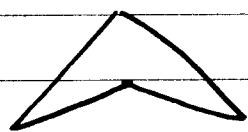


ALL ECLIPSED

(ii) CYCLOBUTANE



IF PLANAR, all C-Hs would be ECLIPSED,
So ring puckers to AVOID TORSIONAL STRAIN



C-C-C angles $\sim 88^\circ$
(worse than 90° , more angle strain)

Total ring strain is $\sim 26 \text{ kcal/mol}$

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

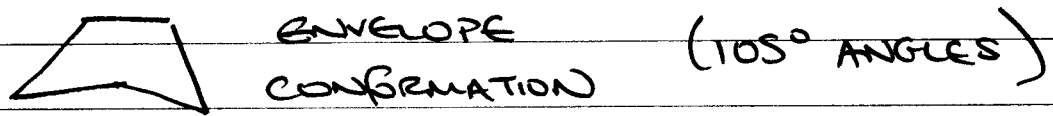
(iii) CYCLOPENTANE



6

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

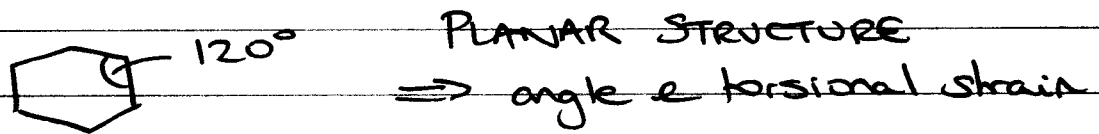


\Rightarrow REDUCES TORSIONAL STRAIN

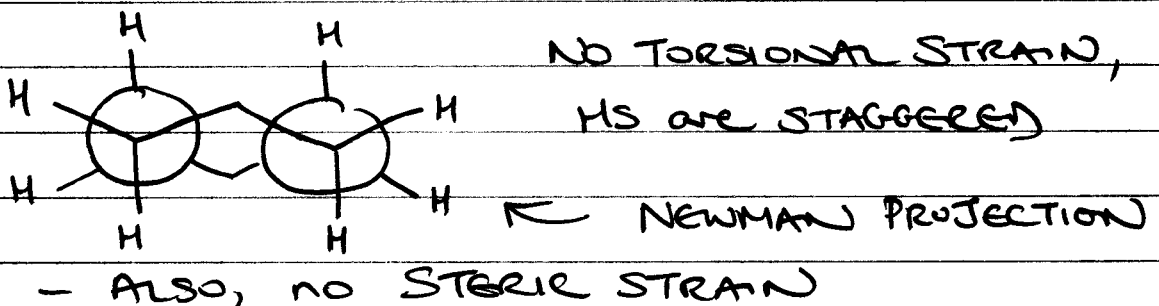
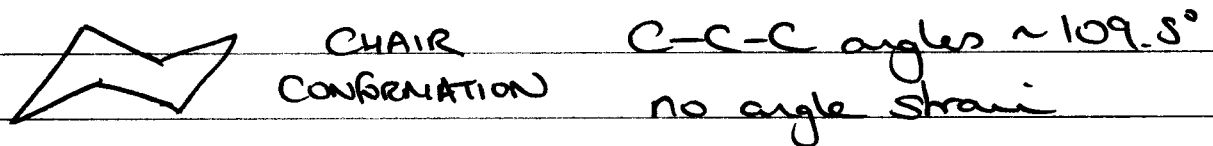
4Cs in PLANE, 1C OUT (EQUILIBRIUM)

Total ring strain ~ 7 kcal/mol

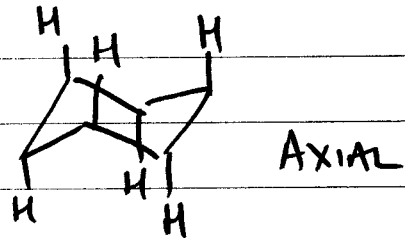
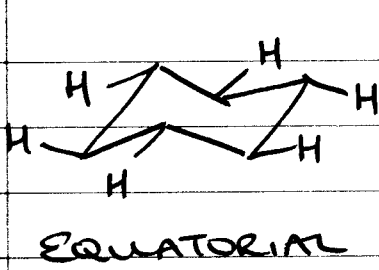
(iv) CYCLOHEXANE



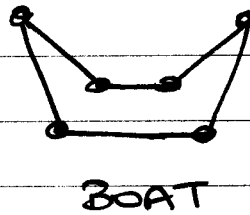
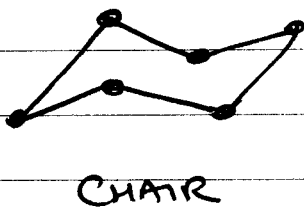
BUT cyclohexane is virtually STRAIN FREE



Two different orientations for C-H bonds



- other conformations



← KNOW THESE TWO

