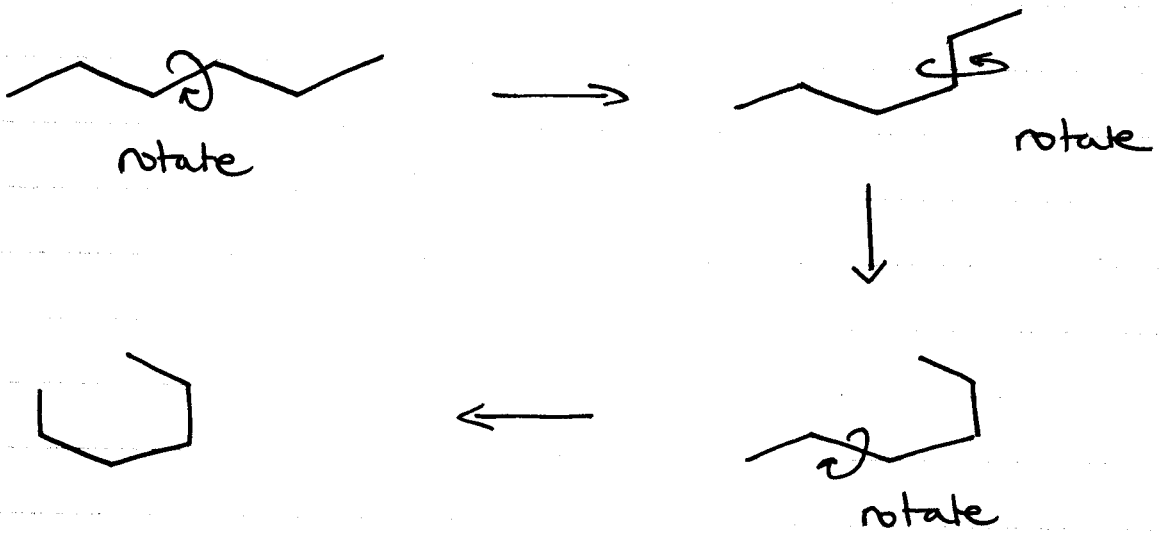
Lec (7) CHEM 30A Jan 24th

- CONFORMATIONAL ANALYSIS
- CYCLOALKANES

HMK: Same problems assigned last time
Read the rest of Chapter 2

CONFORMATIONAL ANALYSIS
- consider HEXANE

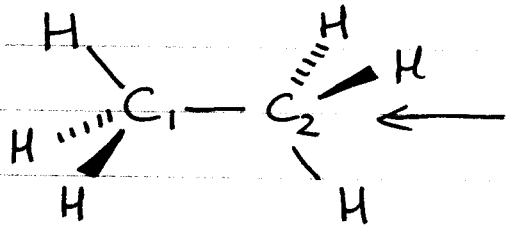


THESE ARE ALL THE SAME COMPOUND

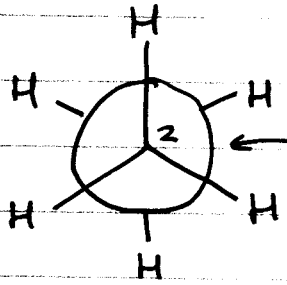
Different arrangements of atoms that result from ONLY single bond rotations are called CONFORMATIONS

At room temperature, all single bonds are constantly rotating —

Consider ETHANE (C_2H_6)



← look from here



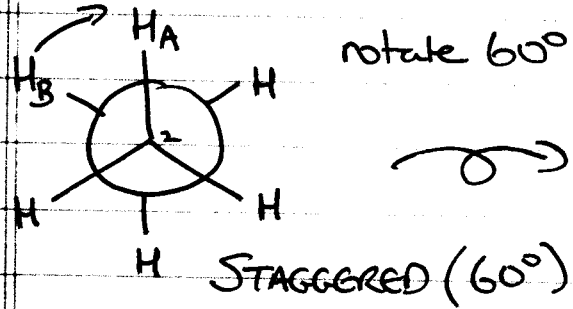
← C_1 is at the back

LOOKING DOWN THE C–C BOND: NEWMAN PROJECTION

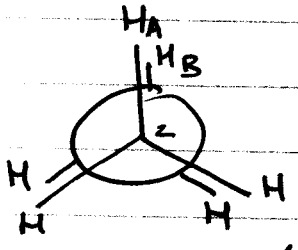
THE TWO METHYL GROUPS ROTATE wrt ONE ANOTHER (0 → 360°)

— INFINITE NUMBER OF CONFORMATIONS

At rt, rate of rotation is ~ 10 BILLION s^{-1}
but rotation is not completely UNHINDERED



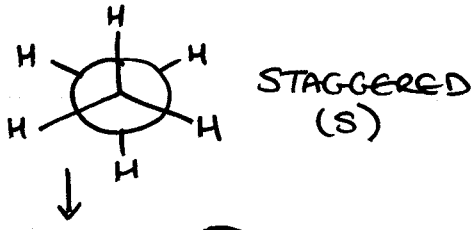
STAGGERED (60°)



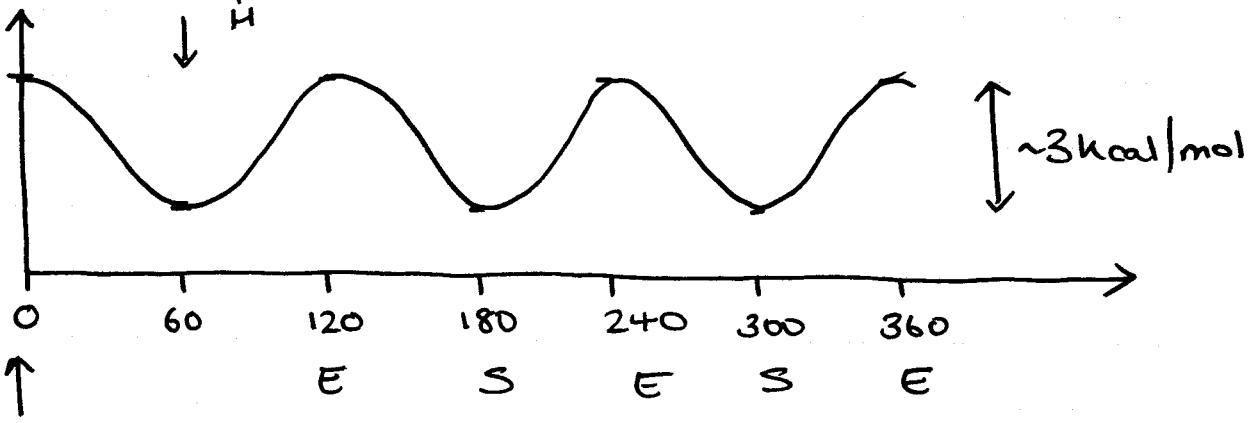
ECLIPSED (0°)

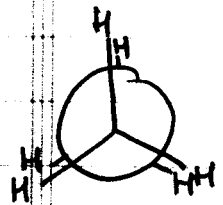
HIGHER IN ENERGY BY ~ 3 kcal mol^{-1}

DIHEDRAL ANGLE (θ) – angle between 2 intersecting planes $H_A C_2 C_1$ & $H_B C_1 C_2$



STAGGERED (S)



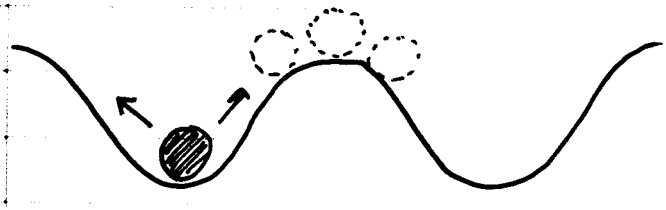


ECLIPSED (E)

ENERGY BARRIER is also called TORSIONAL STRAIN

Any given molecule will spend most of its time in a staggered or nearly staggered conformation (LOWEST ENERGY) and will only briefly pass through the eclipsed conformation on its way to the next staggered conformation.

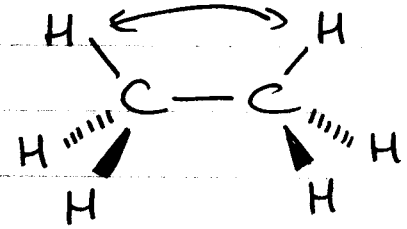
EQUILIBRIUM



with enough energy it will go over the barrier, but it won't spend a lot of time there.

WHY IS THERE A BARRIER?

(i) STERIC INTERACTION?

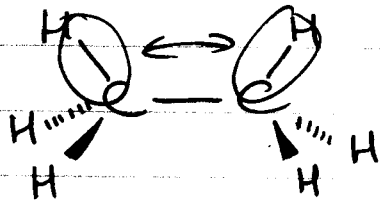


BUT H ATOMS are VERY SMALL

STERICS ACCOUNT FOR ~10% of BARRIER

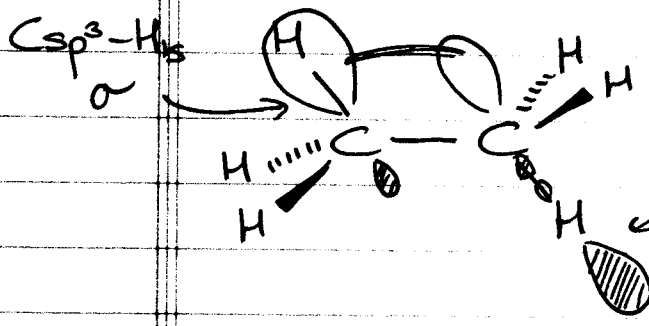
(ii) ELECTRON PAIR REPULSION

TORSIONAL STRAIN



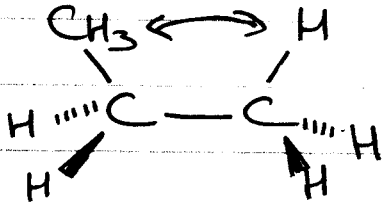
BIGGEST FACTOR

(iii) ATTRACTIVE INTERACTIONS

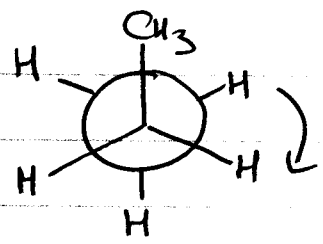


EMPTY ANTIBONDING ORBITAL

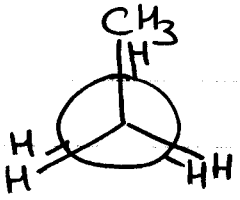
— CONFORMATIONS OF PROPANE?



Bigger repulsive interaction than C–H / C–H



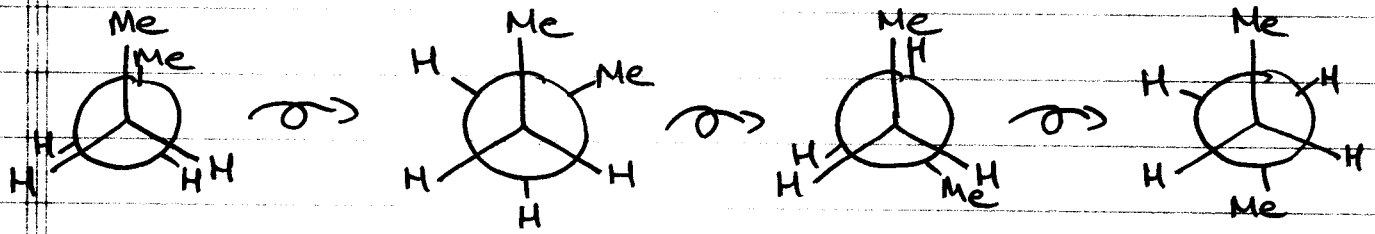
STAGGERED



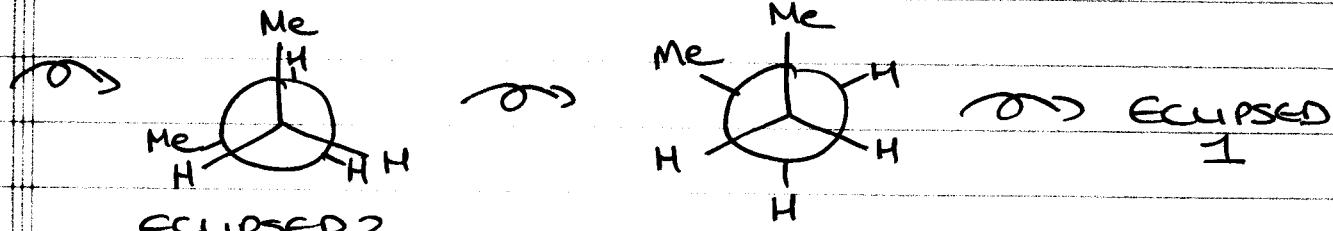
ECLIPSED

Same profile as ETHANE, but HIGHER BARRIER 3.4 kcal/mol

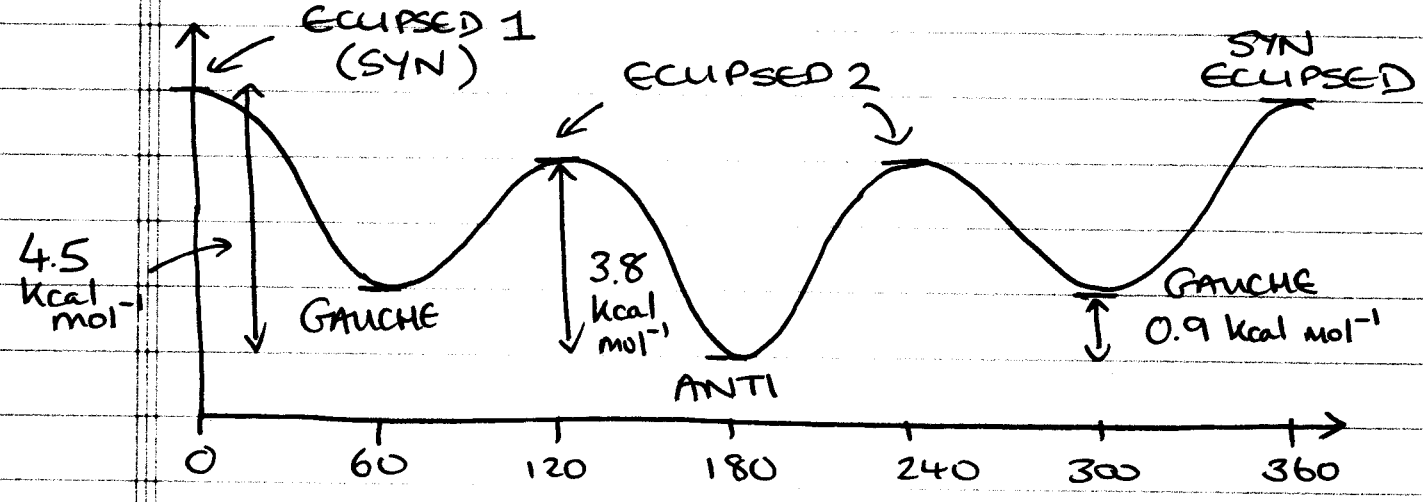
CONFORMATIONS OF BUTANE



ECLIPSED 1 — STAGGERED 1 (GAUCHE) — ECLIPSED 2 — STAGGERED 2 (ANTI)



ECLIPSED 2 (mirror image of other one) — STAGGERED 1 (GAUCHE) (mirror image of other one) — ECLIPSED 1

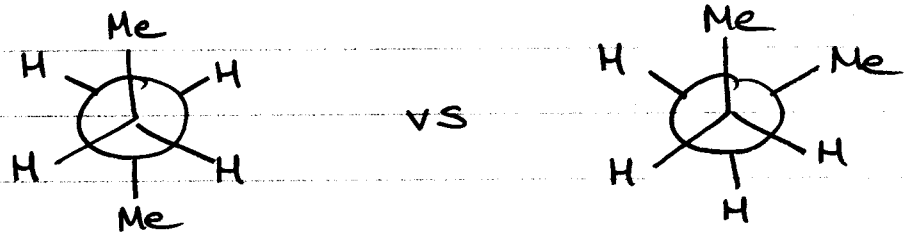


Each eclipsed conformer is a MAXIMA

Each staggered conformer is a MINIMA

BUT different MINIMA/MAXIMA energies

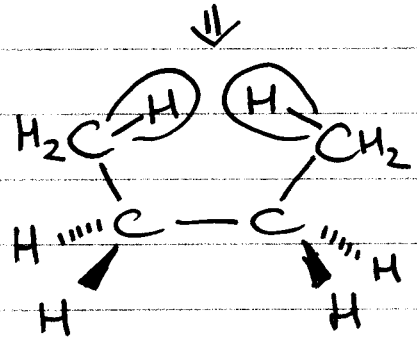
- consider



ANTI (180°) vs GAUCHE (60°)

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

STERIC STRAIN → forcing atoms closer together than atomic radii allow

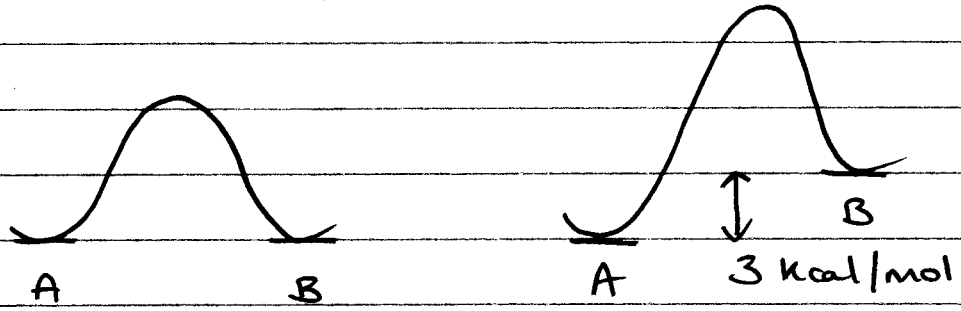


At room temperature, BUTANE is rapidly equilibrating between conformers

~80:20 anti : gauche.

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

At room temperature:



K ← equilibrium constant

$A \rightleftharpoons B$

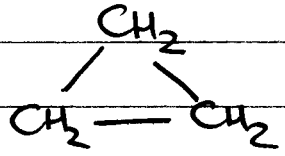
↑ equilibrium arrows

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

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

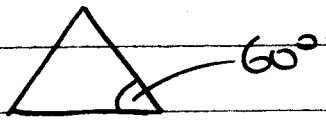
↑ difference in free energy

CYCLOALKANES



cyclopropane

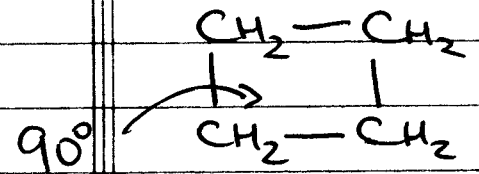
Ring strain of ~28 kcal/mol



TETRAHEDRAL angle is 109.5°

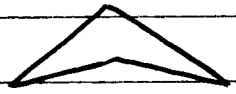
Angle strain is mainly responsible

Also eclipsed C–H bonds (cannot be any other way) ⇒ TORSIONAL STRAIN



cyclobutane

If planar, all C–Hs are eclipsed, so RING PUCKERS to reduce TORSIONAL STRAIN

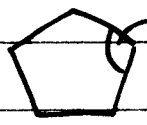


C–C angle ~ 88°

So, ANGLE STRAIN actually increases

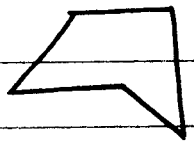
Ring strain is ~ 26 kcal/mol

IN FACT, ALL CYCLOALKANES LARGER THAN CYCLOPROPANE ADOPT NONPLANAR CONFORMATIONS



cyclopentane

PLANAR ⇒ 108°, v. close to 109.5° (TETRAHEDRAL)
very little angle strain, but all C–H bonds would be eclipsed — so/



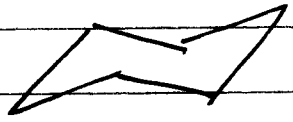
ENVELOPE CONFORMATION
(five equivalent ones – equilibrium)

ring strain is ~ 7 kcal/mol

120° cyclohexane

ANGLE STRAIN & TORSIONAL STRAIN

BUT CYCLOHEXANE is almost STRAIN free

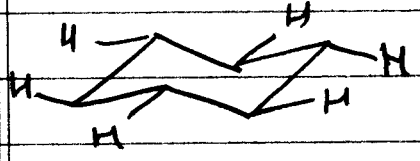


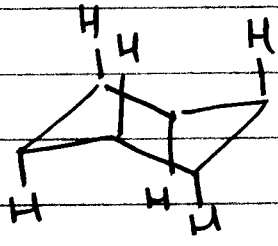
CHAIR CONFORMATION

C–C–C angles ~109.5° NO ANGLE STRAIN

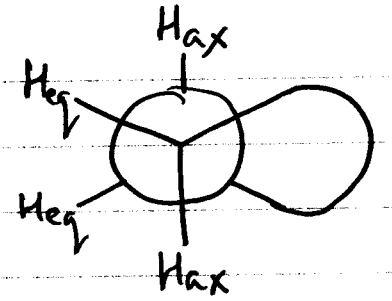
Hs on adjacent Cs are STAGGERED
⇒ NO TORSIONAL STRAIN

EQUATORIAL





AXIAL



NEWMAN PROJECTION down ANY C–C axis.