

LEC ⑧

CHEM 30A

Apr 20th

①

① CYCLOHEXANE

3rd
2.10-2.16, 2.34-2.53

② PROPERTIES OF ALKANES

4th

③ REACTIONS/SOURCES/IMPORTANCE

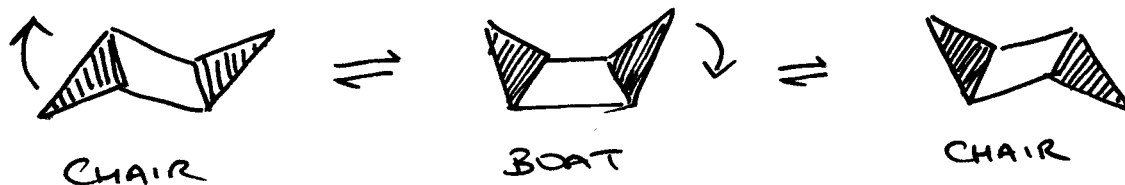
2.11-2.15, 2.36-2.61

④ STEREOCHEMISTRY

READ: 2.9, 2.10, 3.1, 3.2

① CYCLOHEXANE

CHAIR FLIP



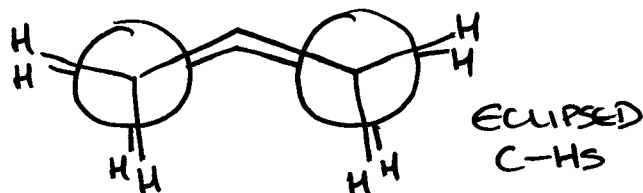
- Switches AXIAL and EQUATORIAL POSITIONS



A CLOSER LOOK AT THE BOAT CONFORMATION



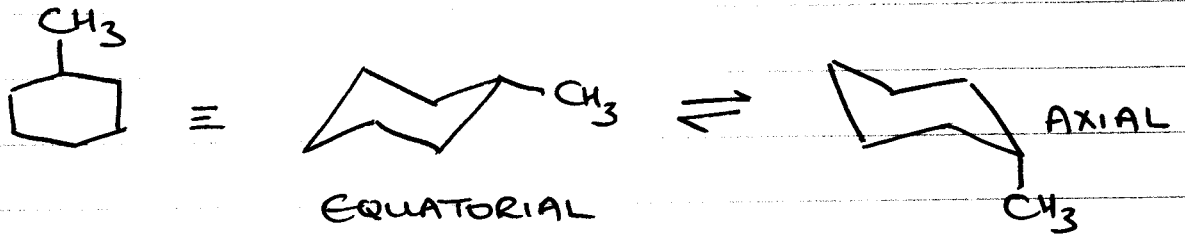
NONBONDED
(STERIC)
INTERACTIONS



ECLIPSED
C-HS

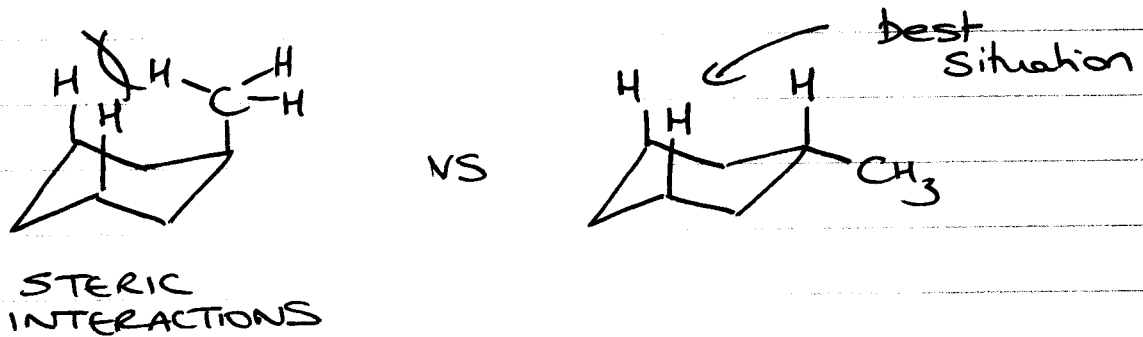
- SUBSTITUTED CYCLOHEXANES

consider METHYL CYCLOHEXANE

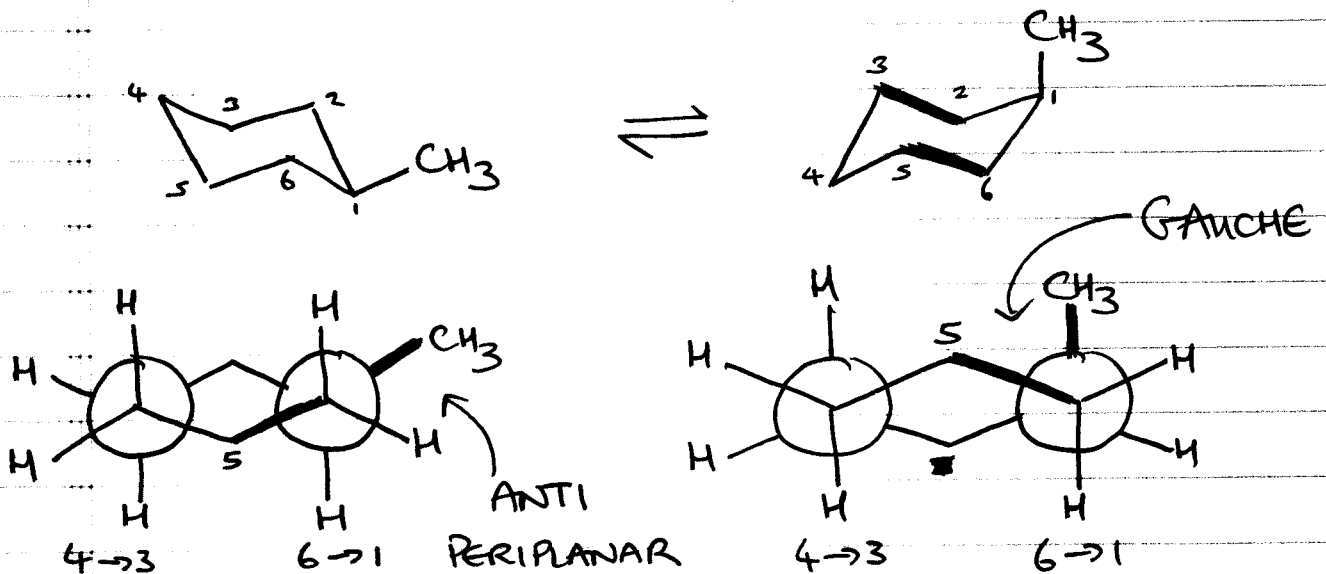


Which is more STABLE?

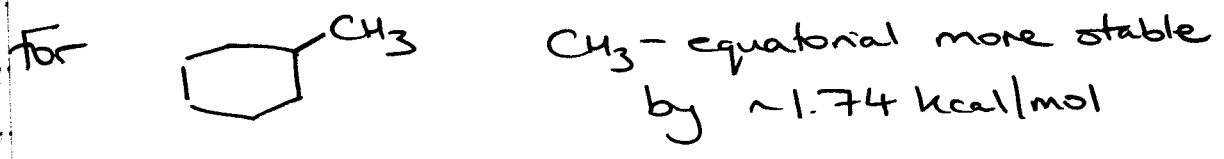
(i) 1,3-DIAXIAL INTERACTIONS



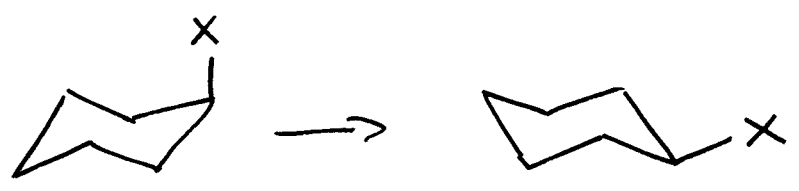
(ii) GAUCHE INTERACTIONS



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



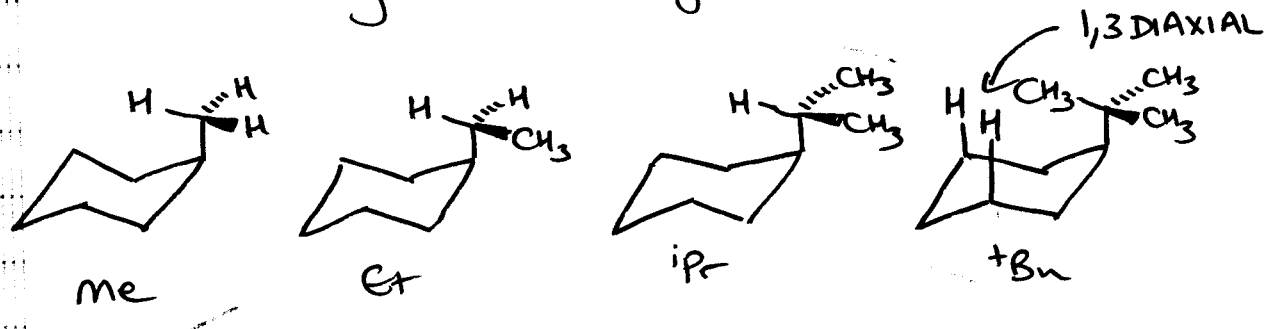
A VALUES \rightarrow measure of preference for equatorial position



NEGATIVE OF ΔG FOR AXIAL \rightarrow EQUATORIAL, SO, A values are usually positive.

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

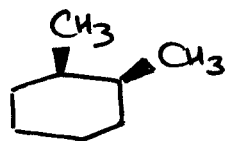
Note relatively small changes for Me, Et, iPr



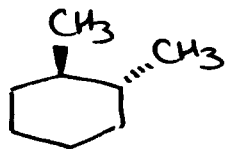
tBu \Rightarrow LOCKING GROUP, OVERWHELMING PREFERENCE FOR EQUATORIAL POSITION



- DISUBSTITUTED CYCLOHEXANES



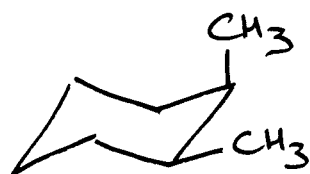
Same side CIS
cis-1,2-dimethylcyclohexane



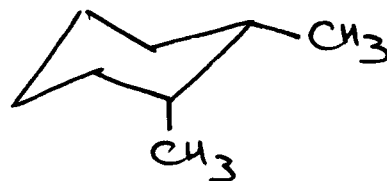
opposite side trans
trans-1,2-dimethylcyclohexane

Note when converting to CHAIR form, \uparrow and \equiv have NOTHING to do with AXIAL/EQUATORIAL, or UP/DOWN

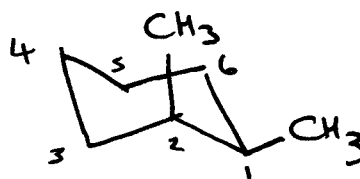
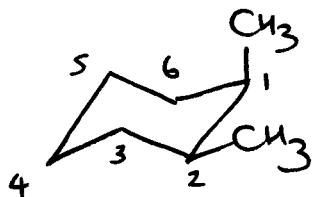
CIS



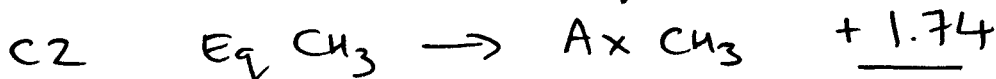
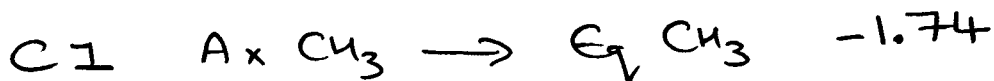
Same as



RING FLIP



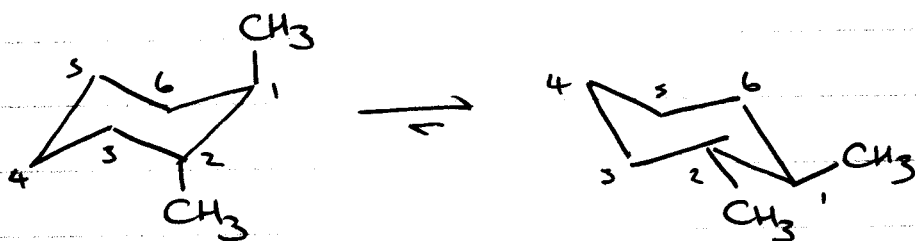
What is ΔG for this equilibrium?



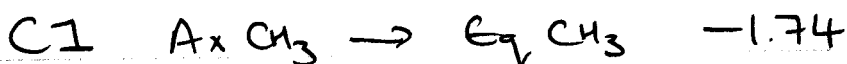
0 kcal/mol

So, 50:50 mixture

trans (opposite sides)



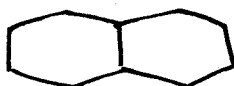
What is ΔG for this equilibrium?



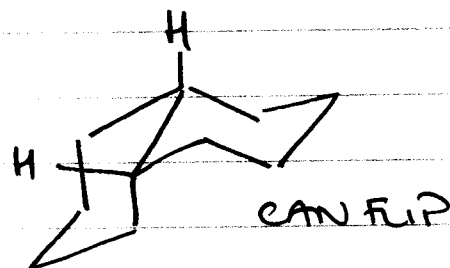
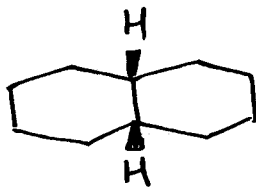
-3.5 kcal/mol^*
(actually -2.6 kcal/mol)

So, conformer w/ two equatorial methyls is favored.

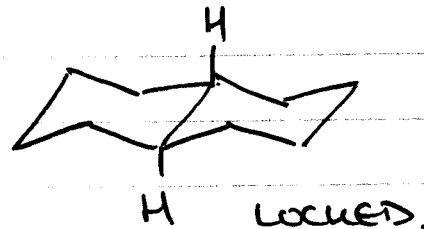
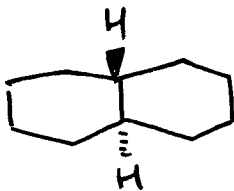
- DECALINS



cis DECALIN



trans DECALIN



② PROPERTIES OF ALKANES

as MW increases, mp & bp increase

INTERMOLECULAR INTERACTIONS

- IONIC
 - HYDROGEN BONDING
 - DIPOLE-DIPOLE
 - DIPOLE-INDUCED DIPOLE
 - INDUCED DIPOLE-INDUCED DIPOLE
- ↳ Dispersion forces / London forces
- ↳ Low MW non polar substances can be liquefied

Decreasing Strength

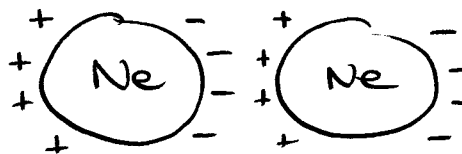
He 4K Ne 27K

Bigger e⁻ clouds, stronger forces



Symmetrical e⁻ density distribution

transient
→
polarisation

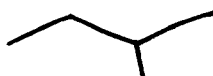


↑
temporary electrostatic interaction

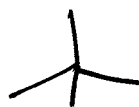
Consider:



bp
36°C



28°C



10°C

CONSTITUTIONAL ISOMERS

↳ more branching →
more compact shape

↳ less surface area →
less molecule/molecule contact

③ Reactions/Sources/Importance

↳ Read Sections 2.9, 2.10

(and look over associated questions)

④ STEREOCHEMISTRY

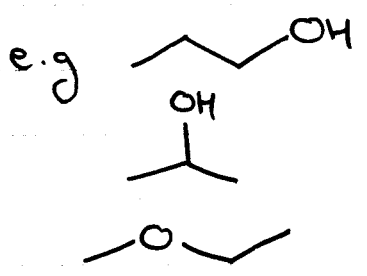
ISOMERS → different compounds with the same molecular formula.

CONSTITUTIONAL ISOMERS

or STEREOISOMERS (configurational isomers)



Different connectivity



Same connectivity of atoms, BUT different geometries

STEREOISOMERS →

ENANTIOMERS

(non superimposable mirror images)



DIASTEREISOMERS (non mirror image stereoisomers)

CONFIGURATIONAL DIASTEREISOMERS

CIS/TRANS DIASTEREISOMERS