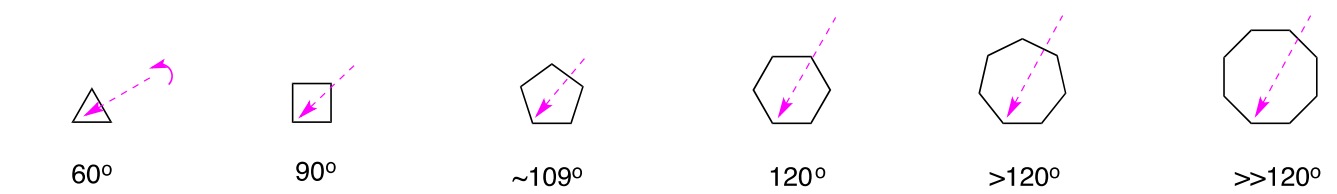


Conformations Of Cyclic Hydrocarbons

A. Introduction

B. Angle Strain



sp^3 hybrid orbitals is around 109° .

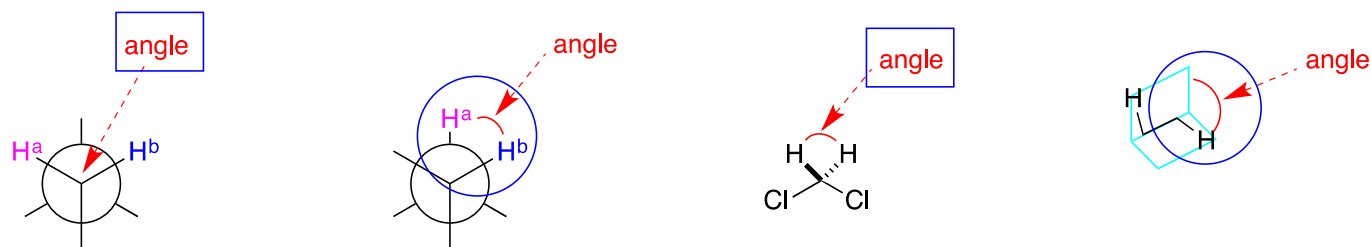
ideal bond angles the molecule has *angle* strain.

relative to the ideal value for sp^3 -hybridization: *cyclopropane / cyclobutane*.

wider than the ideal value for sp^3 -hybridization *if they were flat cyclohexane / cycloheptane / cyclooctane*.

most compressed and expanded angles are: *cyclopropane / cyclooctane*.

C. Torsional Strain



Valence bond angles involve **3** atoms, whereas torsional angles involve **4**.

involves interactions between *e⁻ in bonds* and is *minimized* as

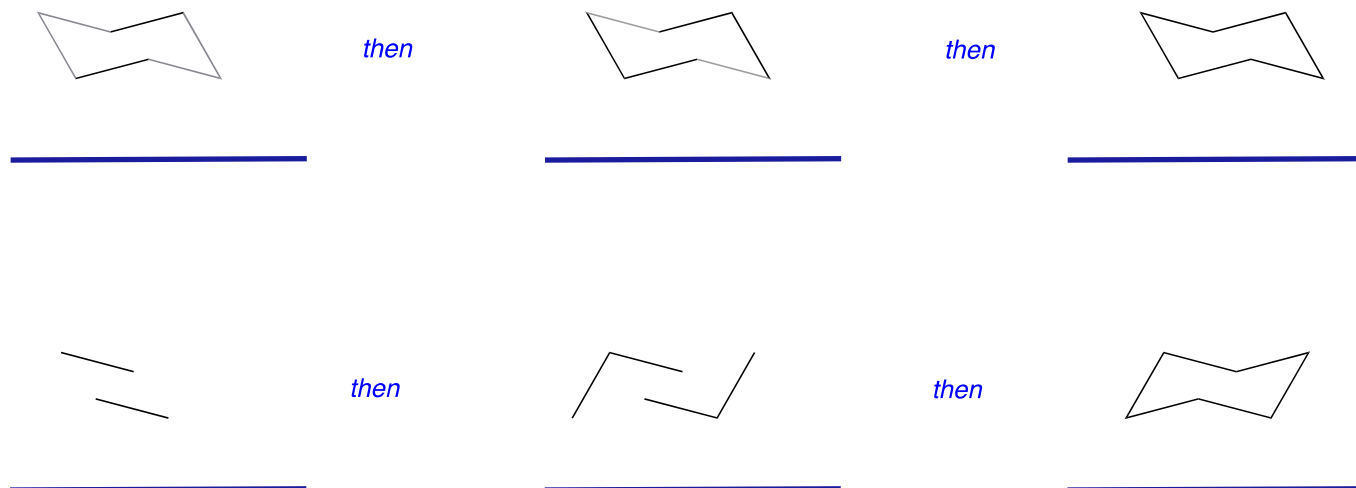
Eclipsed conformations involve high *torsional* strain.

D. Cyclohexanes

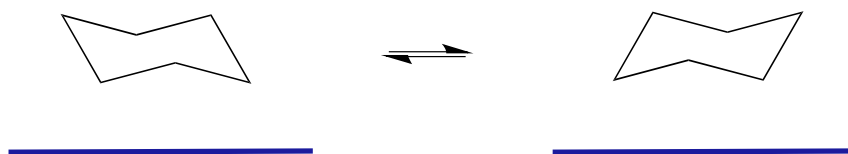
Unsubstituted Cyclohexane

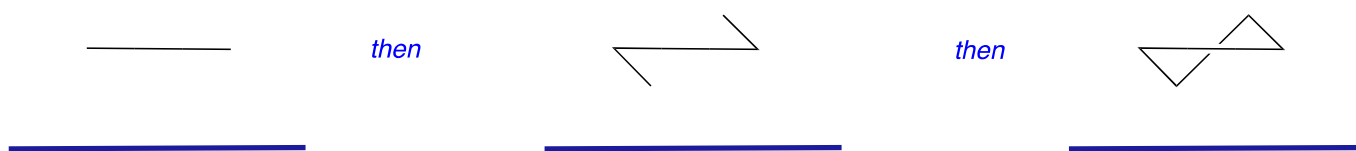
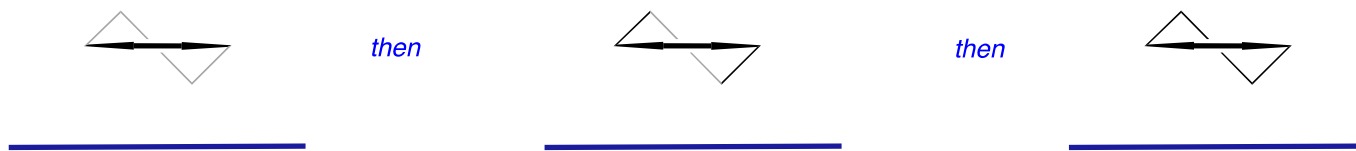
cyclopentane would have *less* angle strain because the internal angle is *closer to* the ideal sp^3 angle.

are *not* flat due to *torsional* strain.

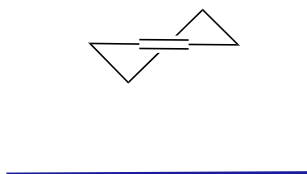


The two conformers have *exactly the same* energies.

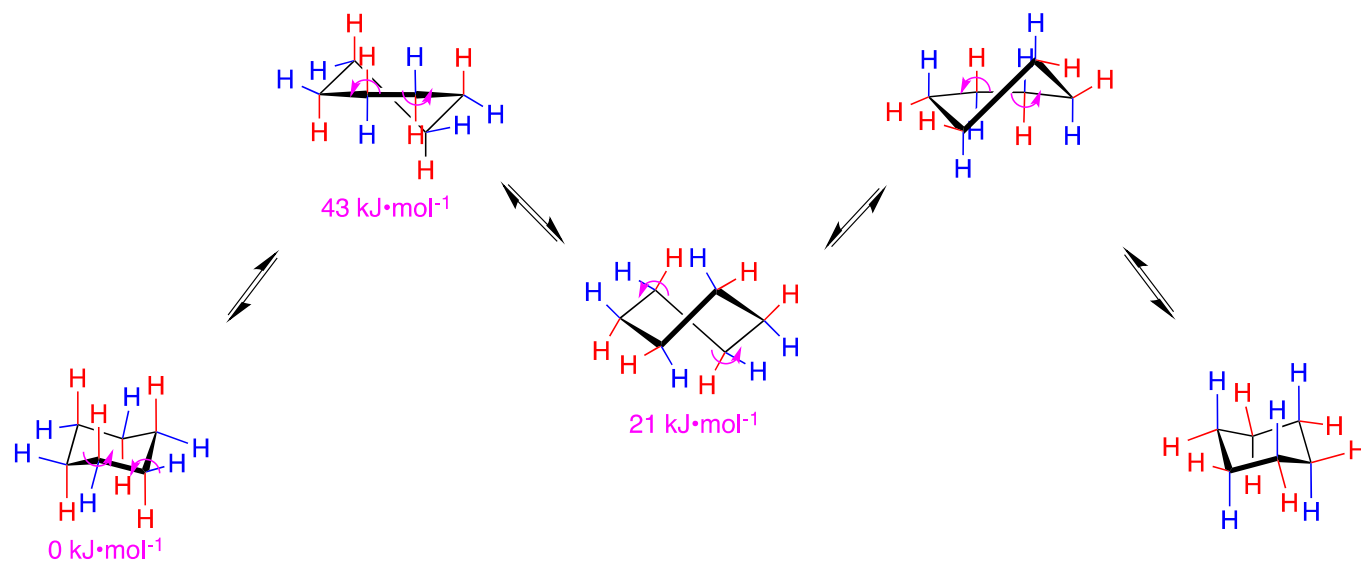


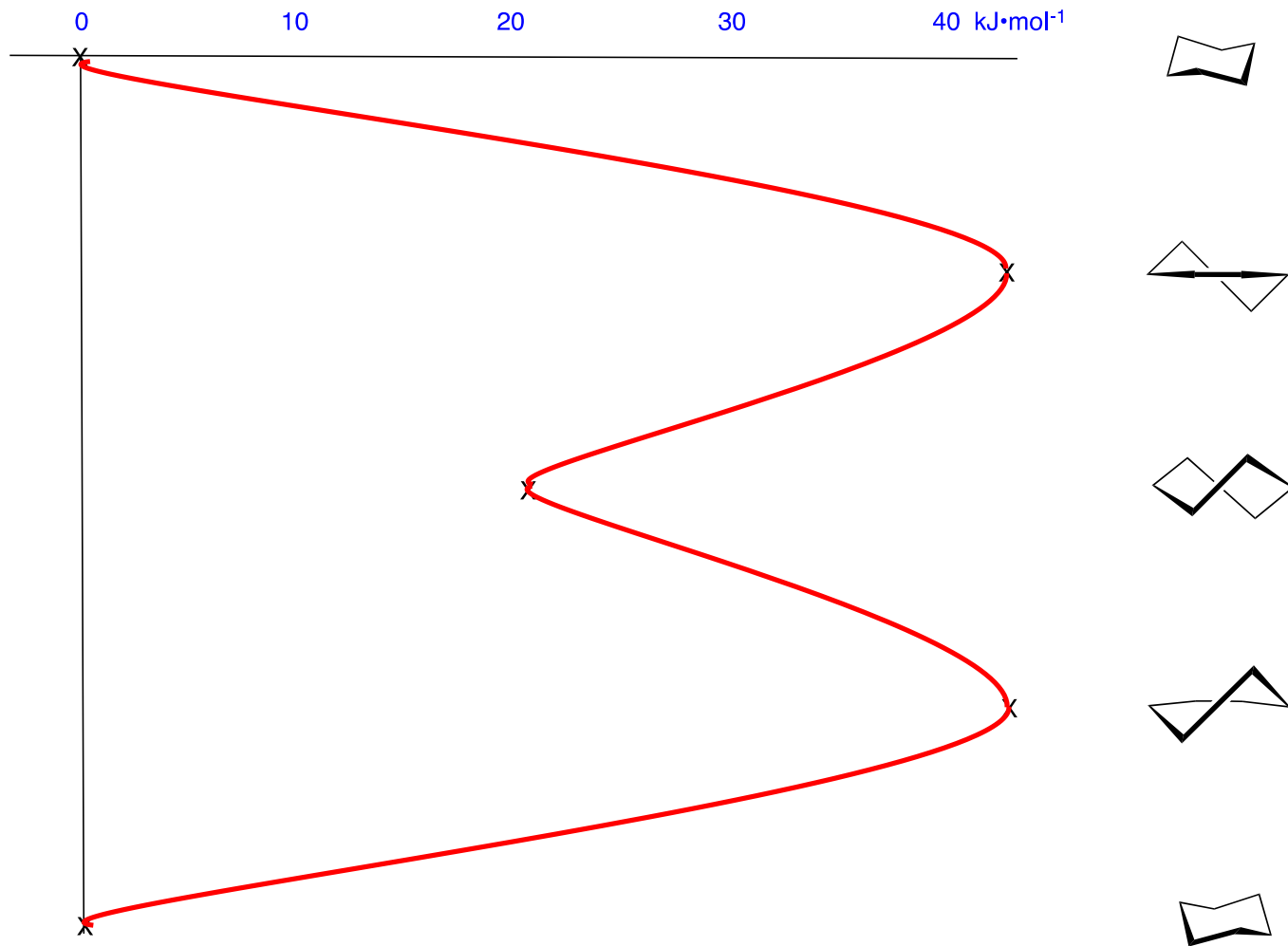


Cyclohexene with a double bond at the front:

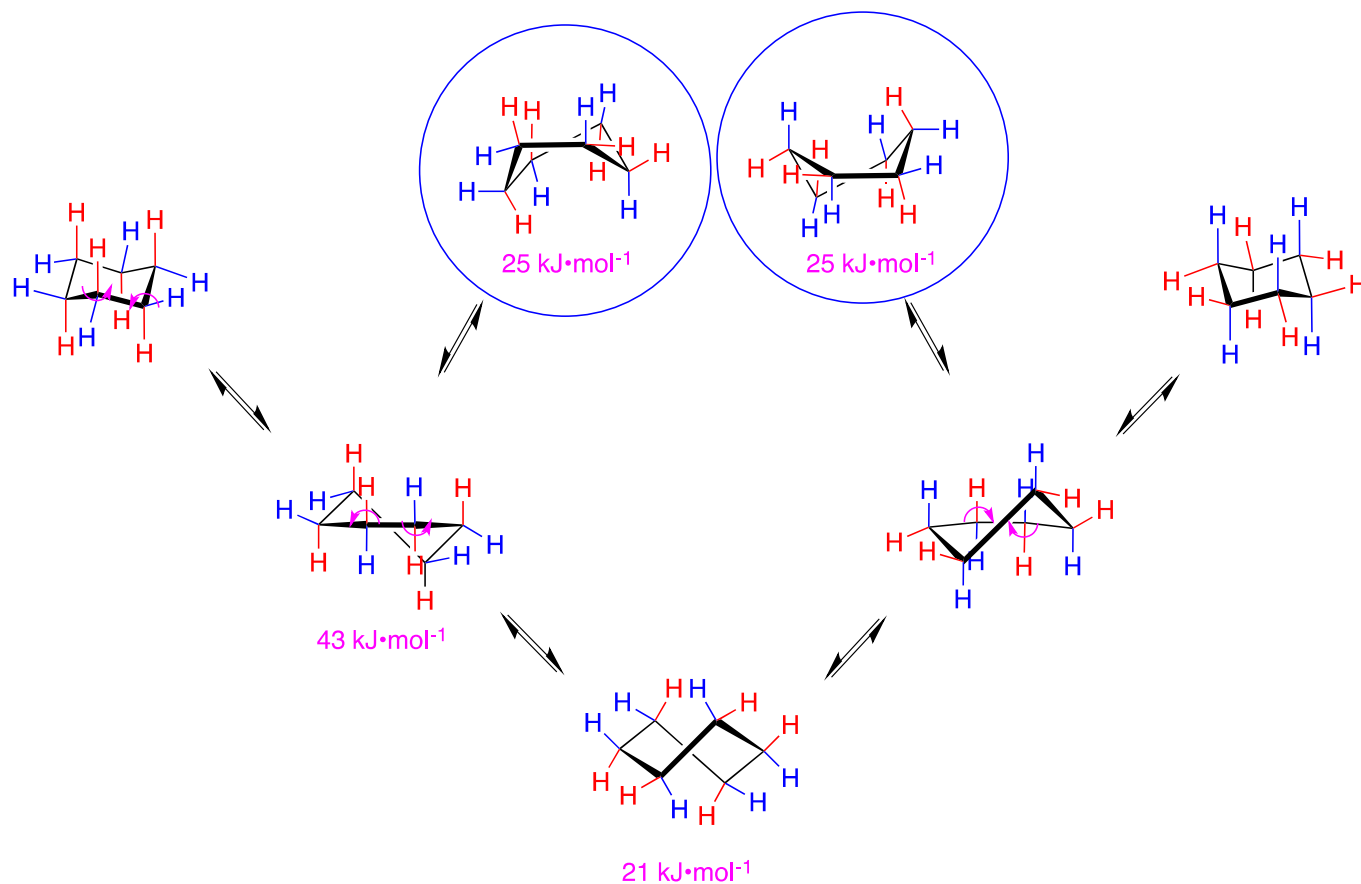


Flipping between chairs involves half-chair transition states and twist-boat intermediates (*Not a solution- understand this diagram and the relationship between conformations and energy levels*):





Boat conformers *are not necessarily* intermediates in flipping

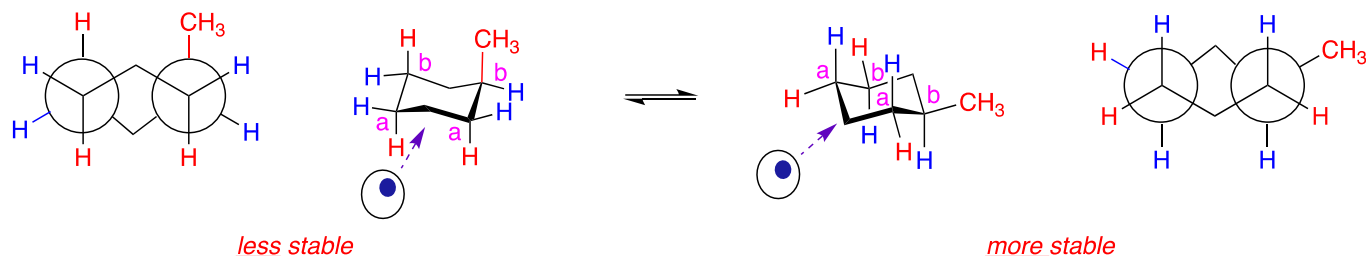


describe interconversion of two chair conformers are *three*-dimensional.

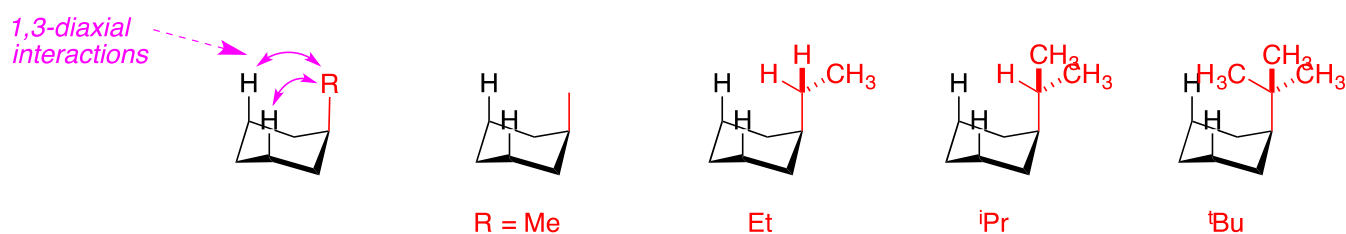


the bonds around C^a – C^b are aligned like the *antiperiplanar* conformation of butane, whereas in the boat form they are like the *gauche* conformer.

Monosubstituted Cyclohexanes



methyl group is axial has **2** H-to-Me gauche interactions, whereas there are **0** similar interactions



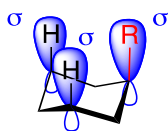
The axial conformer of *tert*-butylcyclohexane is much less stable than the other members of this series because, **unlike for the other substituents, no rotamer (rotation about the σ -bond) around the C-^tBu group allows the methyls to avoid the axial hydrogens.**

equilibrium so much that only the *equatorial* conformer is observed.

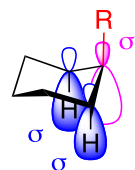
NMR *does* give distinct peaks for the monosubstituted

equilibrate faster than about **1,000** times per second.

C–O bonds have *lower* σ - and σ^* -orbitals

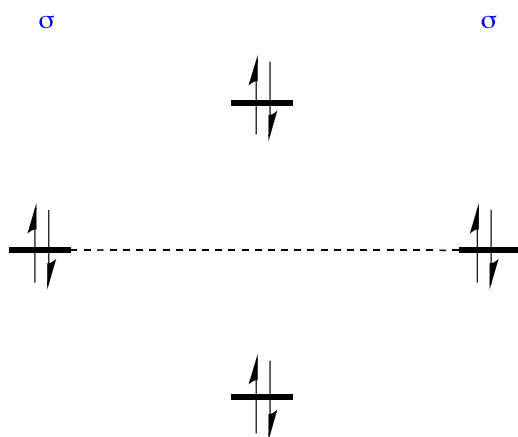


repulsive

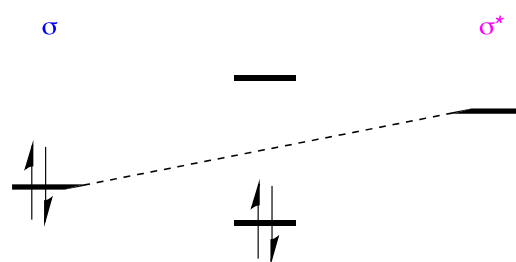


attractive

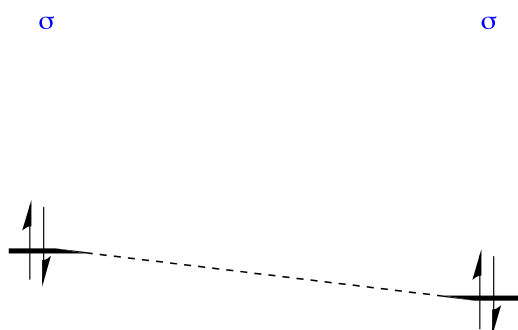
R = Me



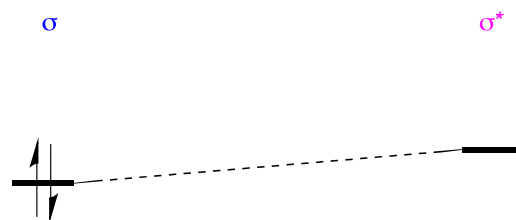
R = Me



R = OMe



R = OMe

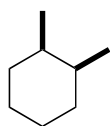
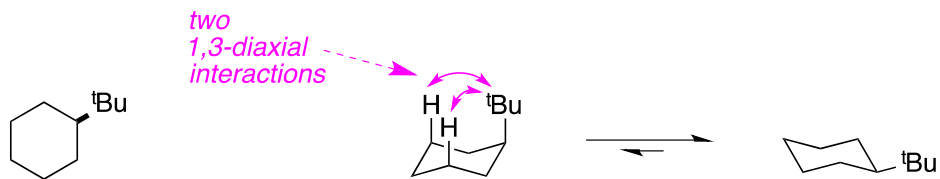


involve *less*
 σ -to- σ^* is *less*

The axial conformer of methoxycyclohexane is slightly more stable than ethylcyclohexane because C–O bonds have lower σ^* -orbitals, thus the energy gap between this and the C–H σ -orbital is less and this stabilizes σ -to- σ^* interaction.

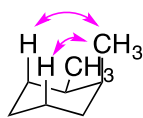
Disubstituted Cyclohexanes

example

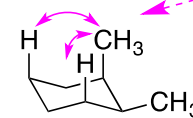


how many 1,3-diaxial interactions?

two

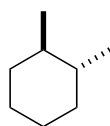


equilibrium position

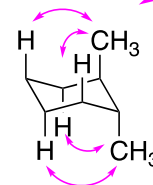
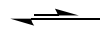
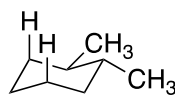


how many 1,3-diaxial interactions?

two

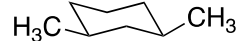
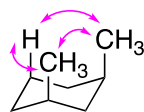


no 1,3-diaxial interaction

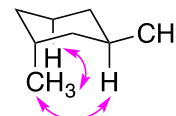
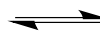
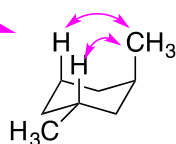


four 1,3-diaxial interactions

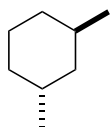
three 1,3-diaxial interactions

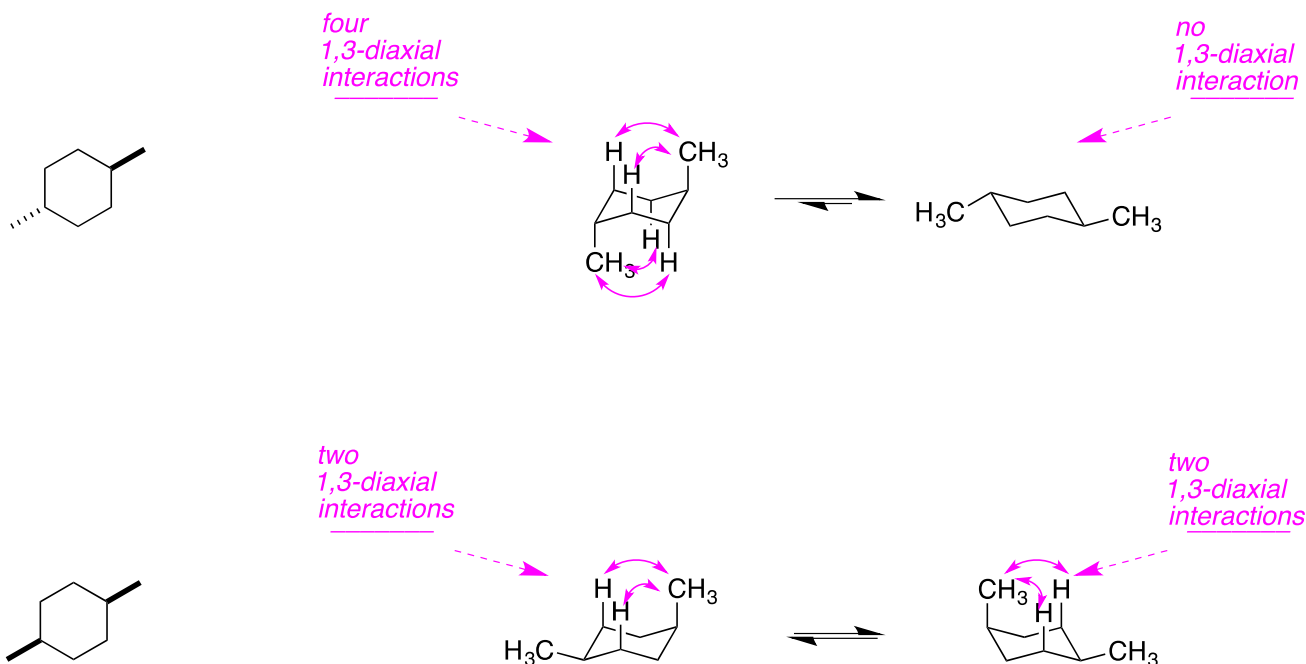


two 1,3-diaxial interactions



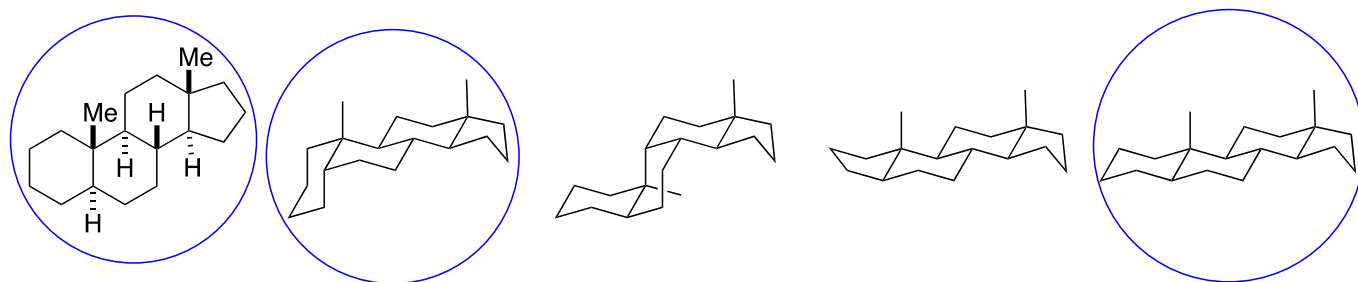
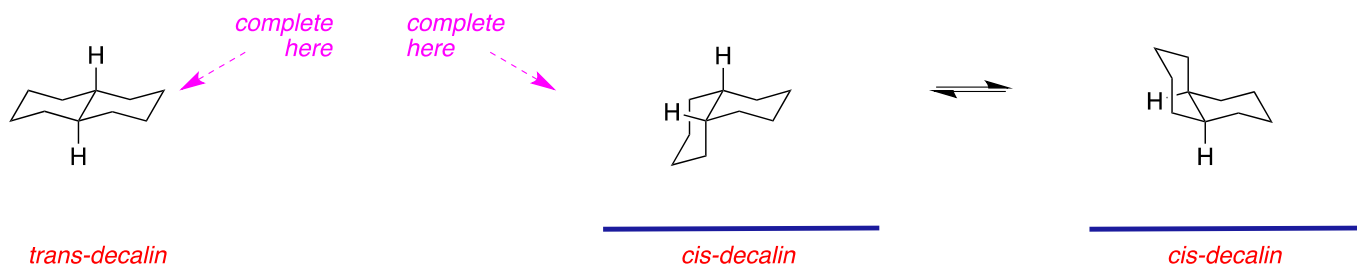
two 1,3-diaxial interactions





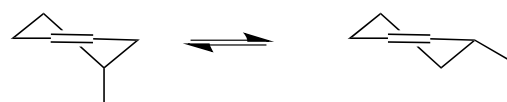
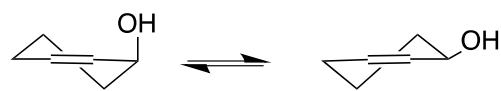
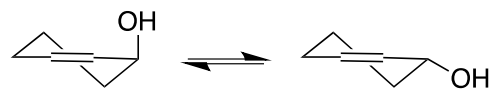
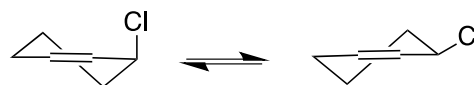
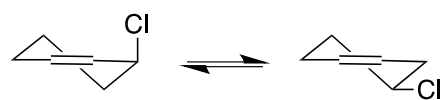
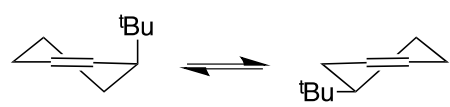
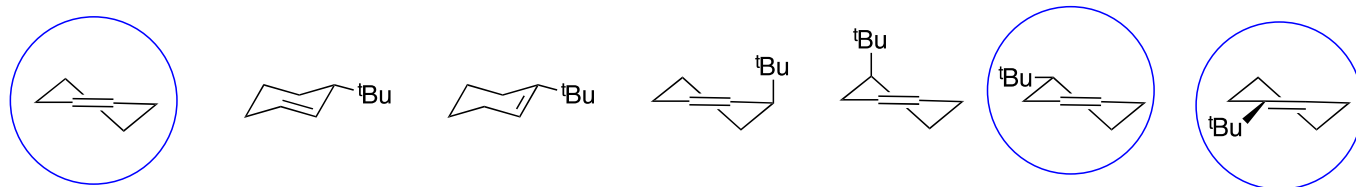
Decalins

Decalins feature two cyclohexane rings sharing *a bond*; look up the structure in Wiki.

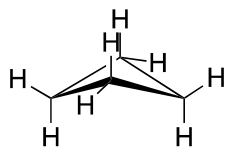


None of the above structures can undergo a ring flip. If ring **A** were flipped, ring **B** would have to flip too, but it cannot because **B/C** is a *trans*-decalin, and *trans*-decalins cannot flip.

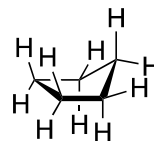
Cyclohexenes



E. Other Rings



cyclobutane



cyclopentane

In solution these molecules *do* rapidly interchange (on the NMR time-scale)

Three membered rings in cyclopropanes are *rigid and flat*.

Cyclopropane substituents are *eclipsed* relative to each other.