3.4

The Shapes of Cycloalkanes: Planar or Nonplanar?

Adolf von Baeyer (19th century)

assumed cycloalkanes are planar polygons

distortion of bond angles from 109.5° gives angle strain to cycloalkanes with rings either smaller or larger than cyclopentane

Baeyer deserves credit for advancing the idea of angle strain as a destabilizing factor.

But Baeyer was incorrect in his belief that cycloalkanes were planar.

Types of Strain

- *Torsional strain*

  strain that results from eclipsed bonds

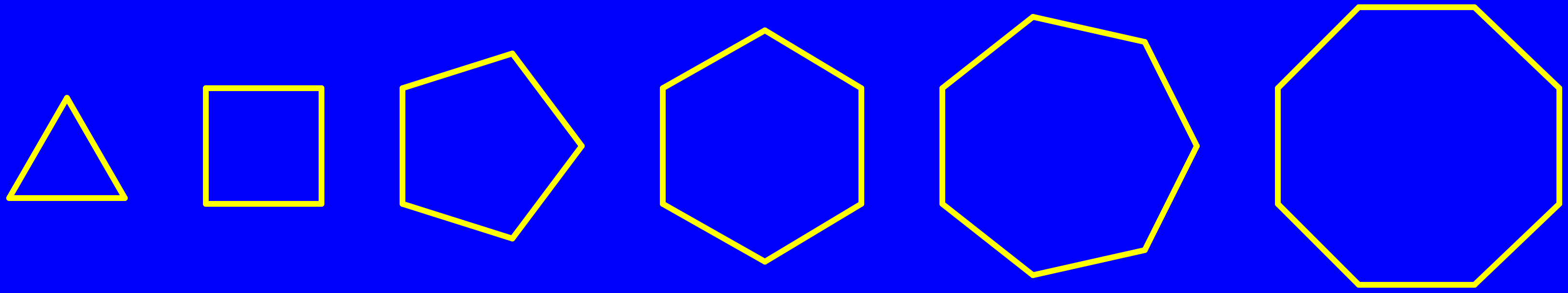
- *van der Waals strain (steric strain)*

  strain that results from atoms being too close together

- *angle strain*

  strain that results from distortion of bond angles from normal values

Measuring Strain in Cycloalkanes

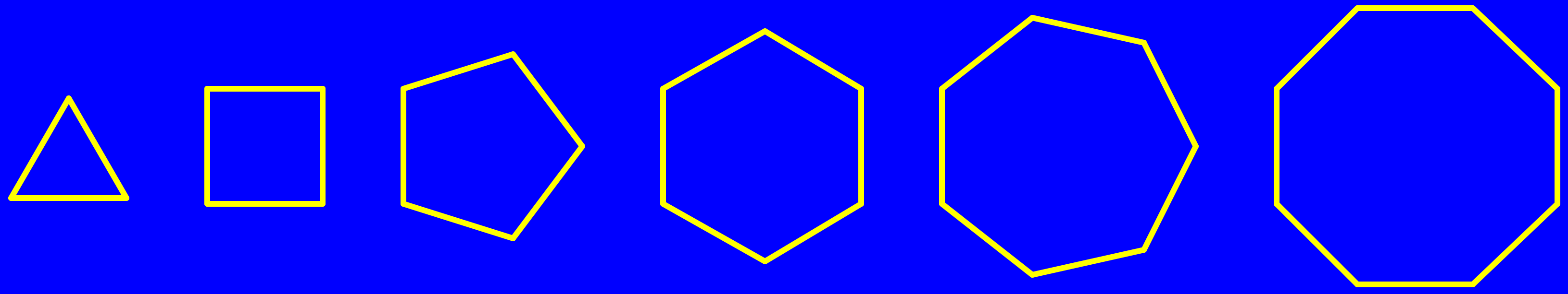


Heats of combustion can be used to compare stabilities of isomers.

But cyclopropane, cyclobutane, etc. are not isomers.

All heats of combustion increase as the number of carbon atoms increase.

Measuring Strain in Cycloalkanes



Therefore, divide heats of combustion by number of carbons and compare heats of combustion on a "per CH_2 group" basis.

Heats of Combustion in Cycloalkanes

Cycloalkane	kJ/mol	Per CH_2
Cyclopropane	2,091	697
Cyclobutane	2,721	681
Cyclopentane	3,291	658
Cyclohexane	3,920	653
Cycloheptane	4,599	657
Cyclooctane	5,267	658
Cyclononane	5,933	659
Cyclodecane	6,587	659

Heats of Combustion in Cycloalkanes

According to Baeyer, cyclopentane should have less angle strain than cyclohexane.

Cycloalkane	kJ/mol	Per CH_2
Cyclopentane	3,291	658
Cyclohexane	3,920	653

The heat of combustion per CH_2 group is less for cyclohexane than for cyclopentane.

Therefore, cyclohexane has less strain than cyclopentane.

Adolf von Baeyer (19th century)

assumed cycloalkanes are planar polygons

distortion of bond angles from 109.5° gives angle strain to cycloalkanes with rings either smaller or larger than cyclopentane

Baeyer deserves credit for advancing the idea of angle strain as a destabilizing factor.

But Baeyer was incorrect in his belief that cycloalkanes were planar.

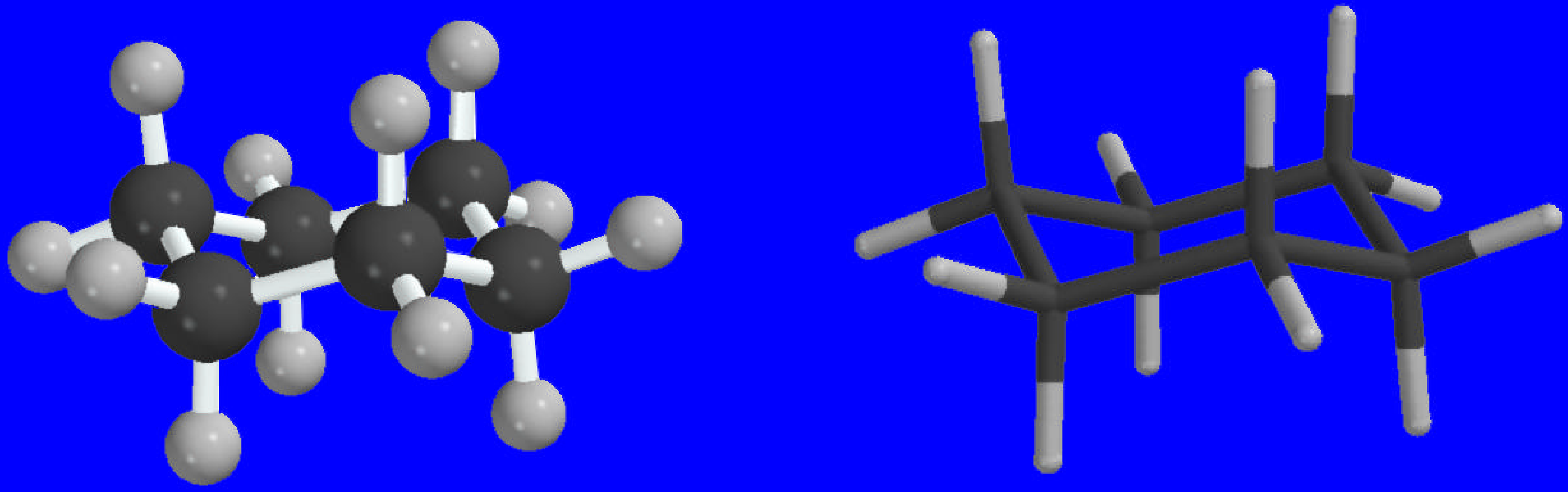
3.5

Conformations of Cyclohexane

heat of combustion suggests that angle strain is unimportant in cyclohexane

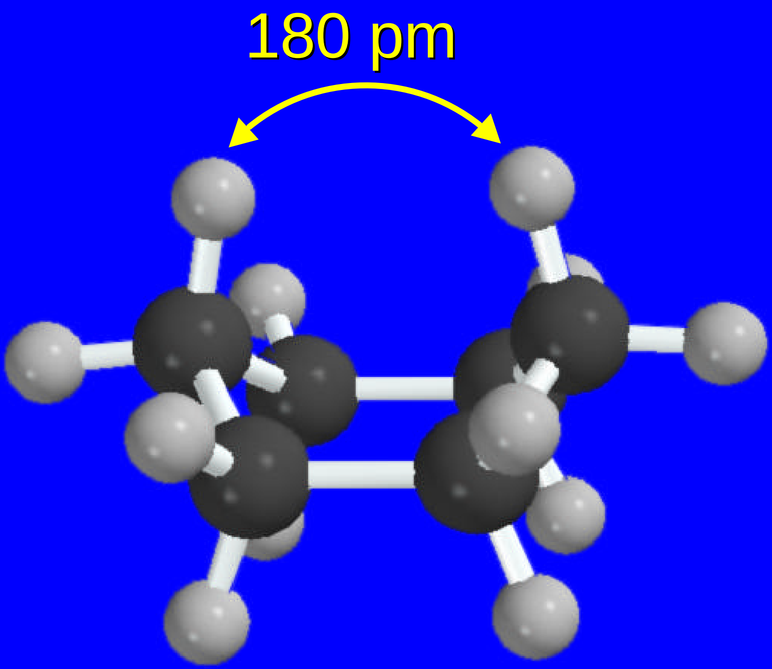
tetrahedral bond angles require nonplanar geometries

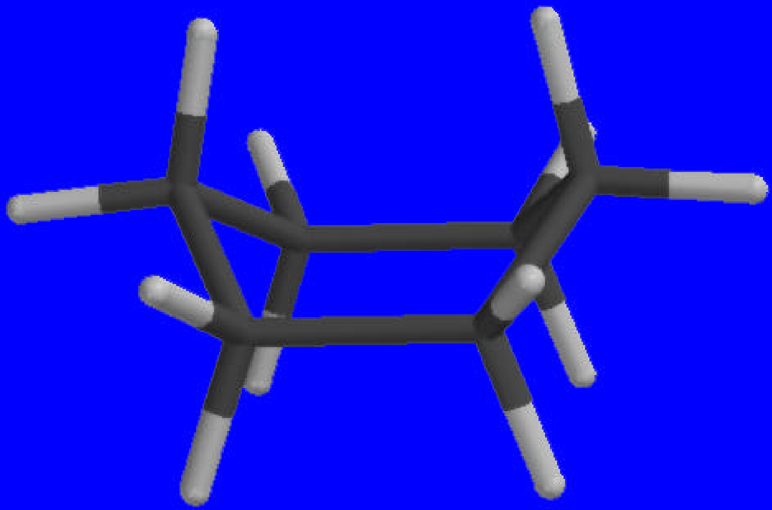
Chair is the most stable conformation of cyclohexane



All of the bonds are staggered and the
bond angles at carbon are close to tetrahedral.

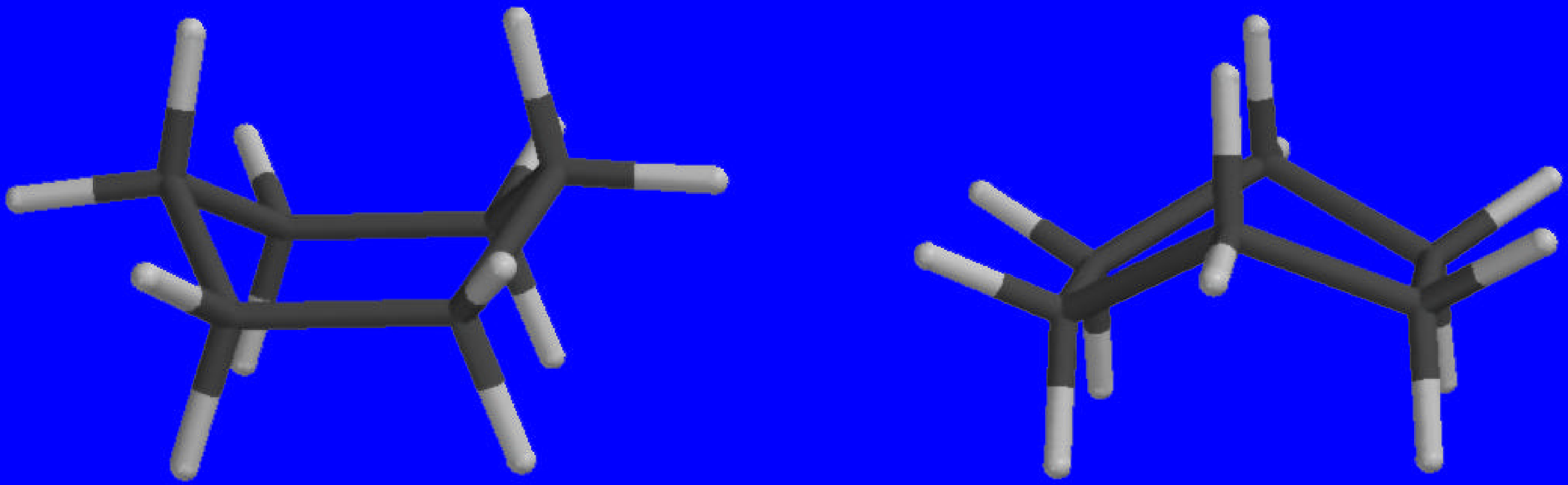
Boat conformation is less stable than the chair





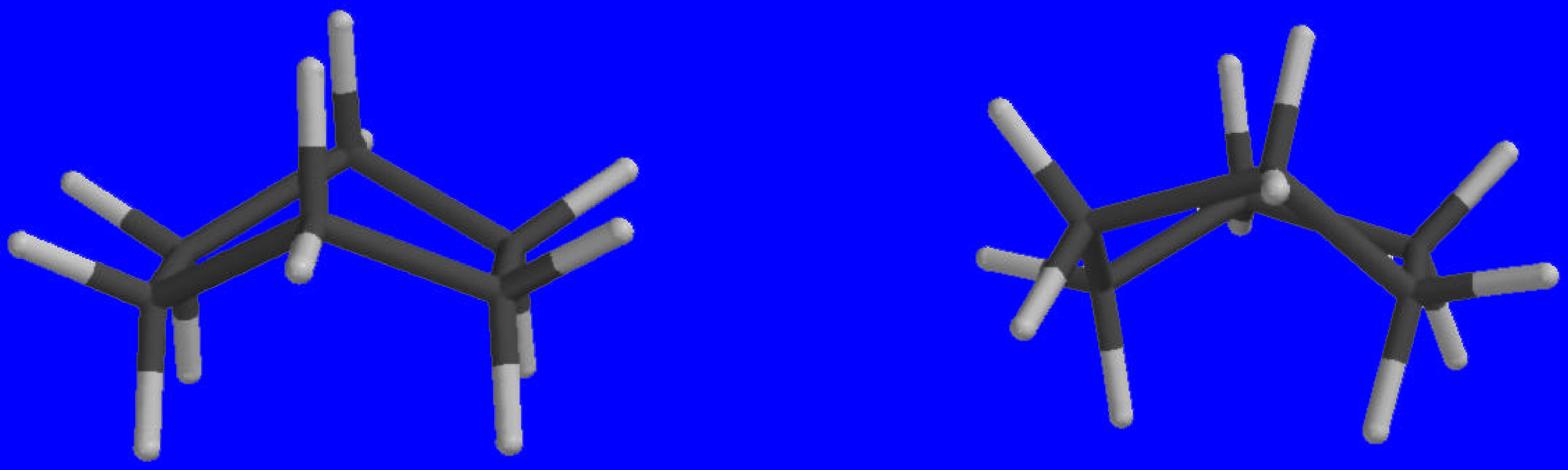
All of the bond angles are close to tetrahedral but close contact between flagpole hydrogens causes van der Waals strain in boat.

Boat conformation is less stable than the chair



Eclipsed bonds bonds gives torsional strain to boat.

Skew boat is slightly more stable than boat



Less van der Waals strain and less torsional strain in skew boat.

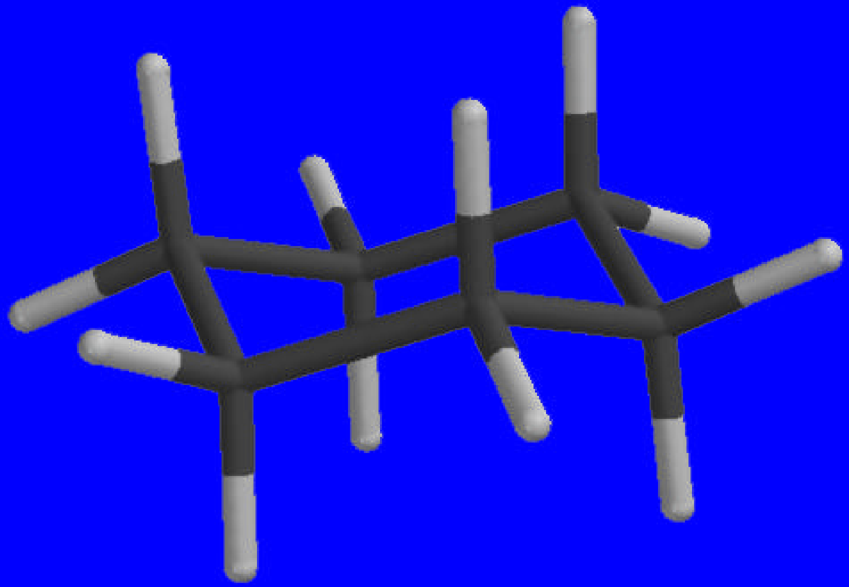
Generalization

the chair conformation of cyclohexane is the most stable conformation and derivatives of cyclohexane almost always exist in the chair conformation

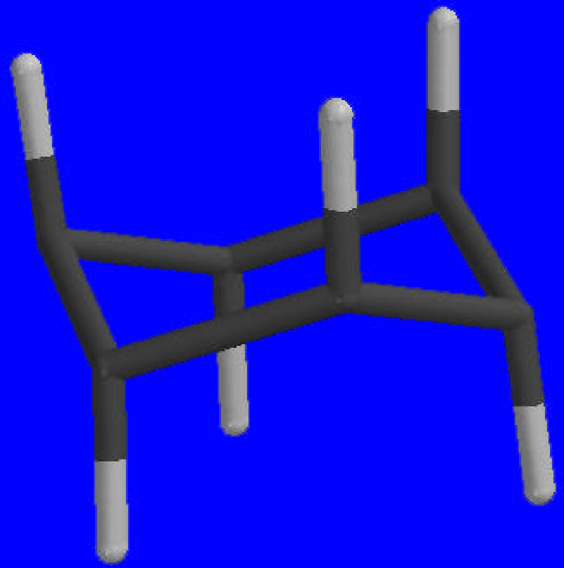
3.6

Axial and Equatorial Bonds in Cyclohexane

The 12 bonds to the ring can be divided into two sets of 6.

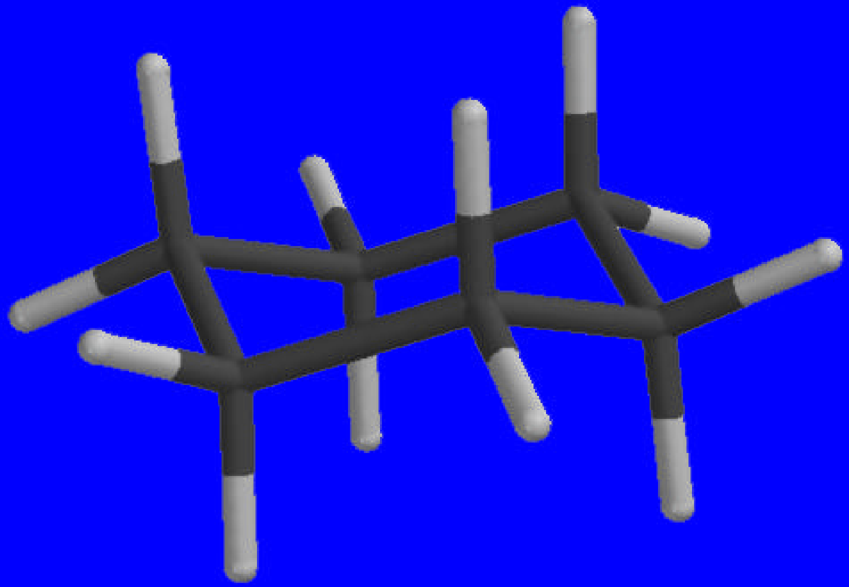


6 Bonds are axial

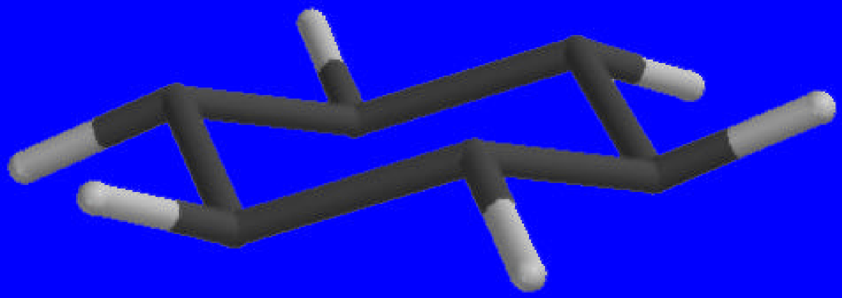


Axial bonds point "north and south"

The 12 bonds to the ring can be divided into two sets of 6.



6 Bonds are equatorial

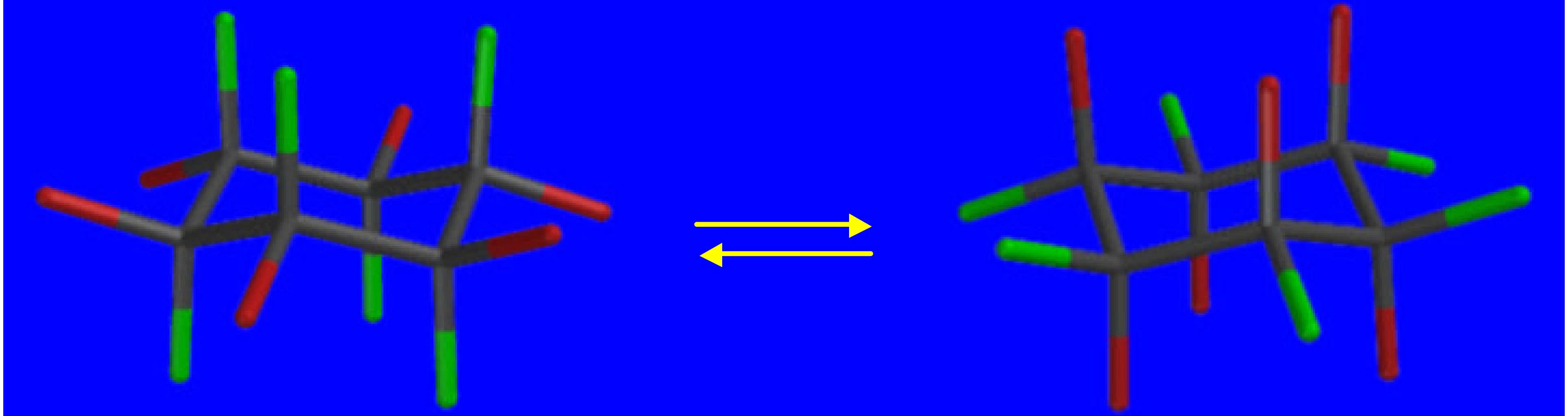


Equatorial bonds lie along the equator

3.7

Conformational Inversion (Ring-Flipping) in Cyclohexane

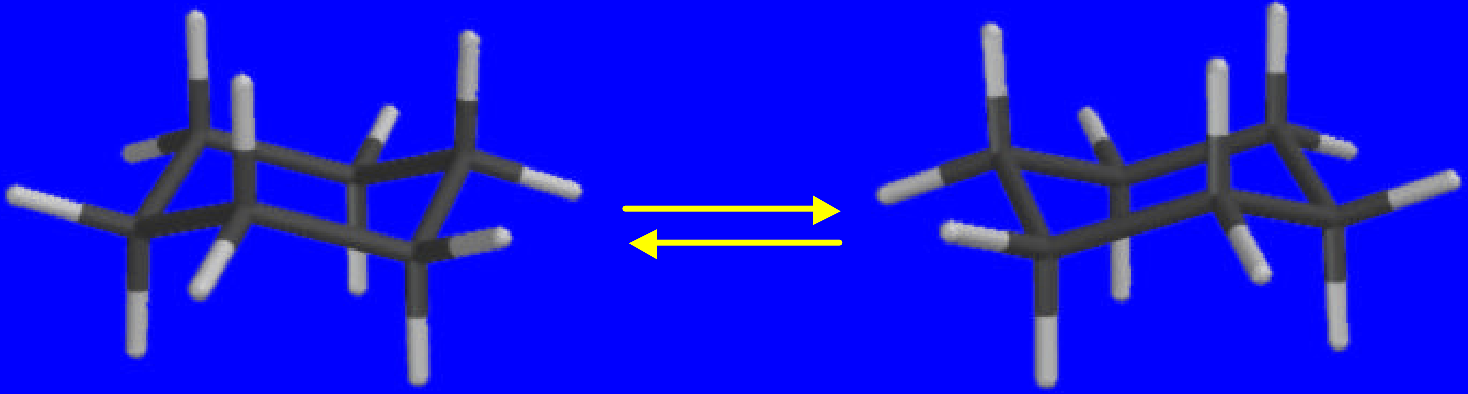
Conformational Inversion

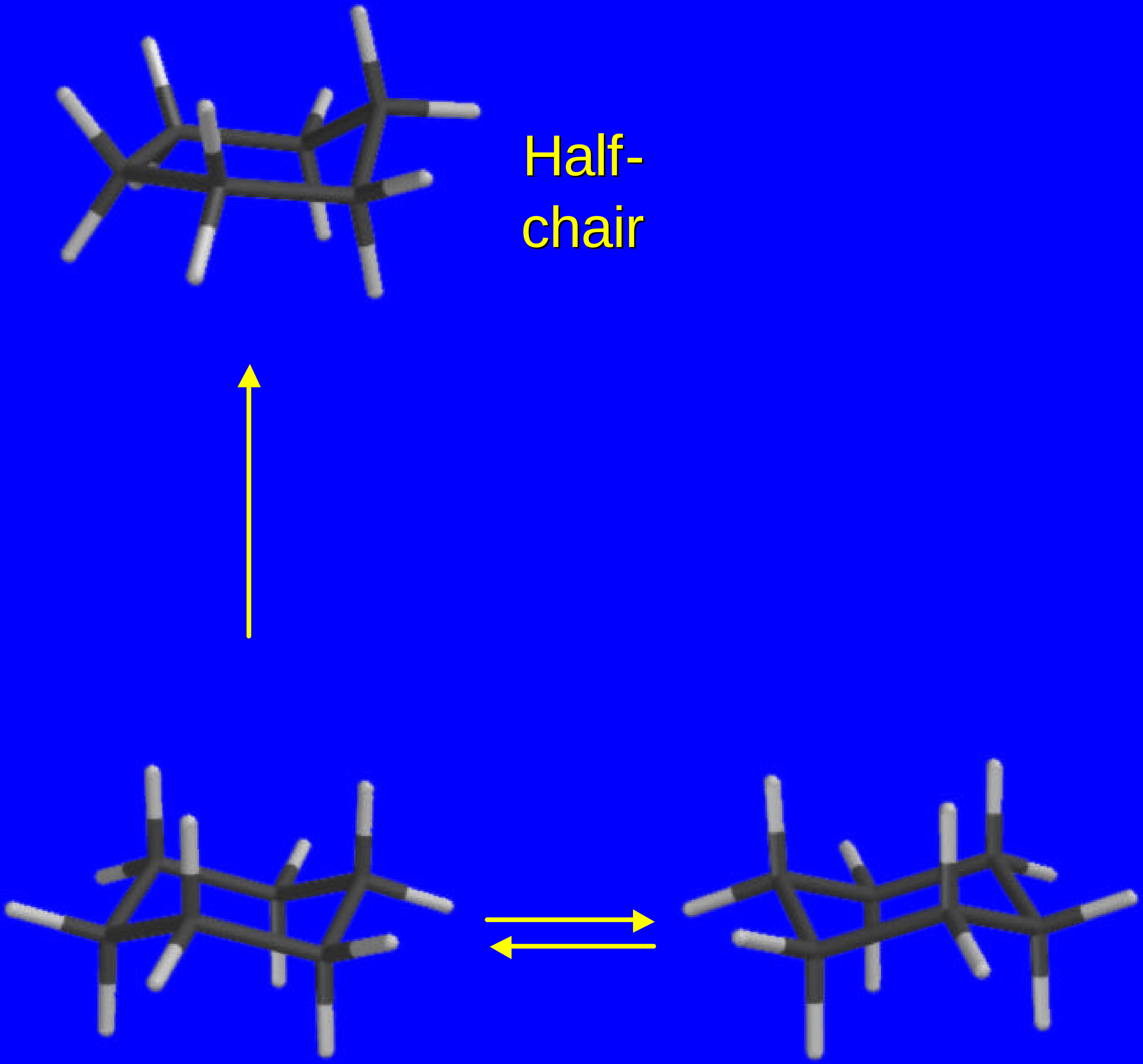


chair-chair interconversion (ring-flipping)

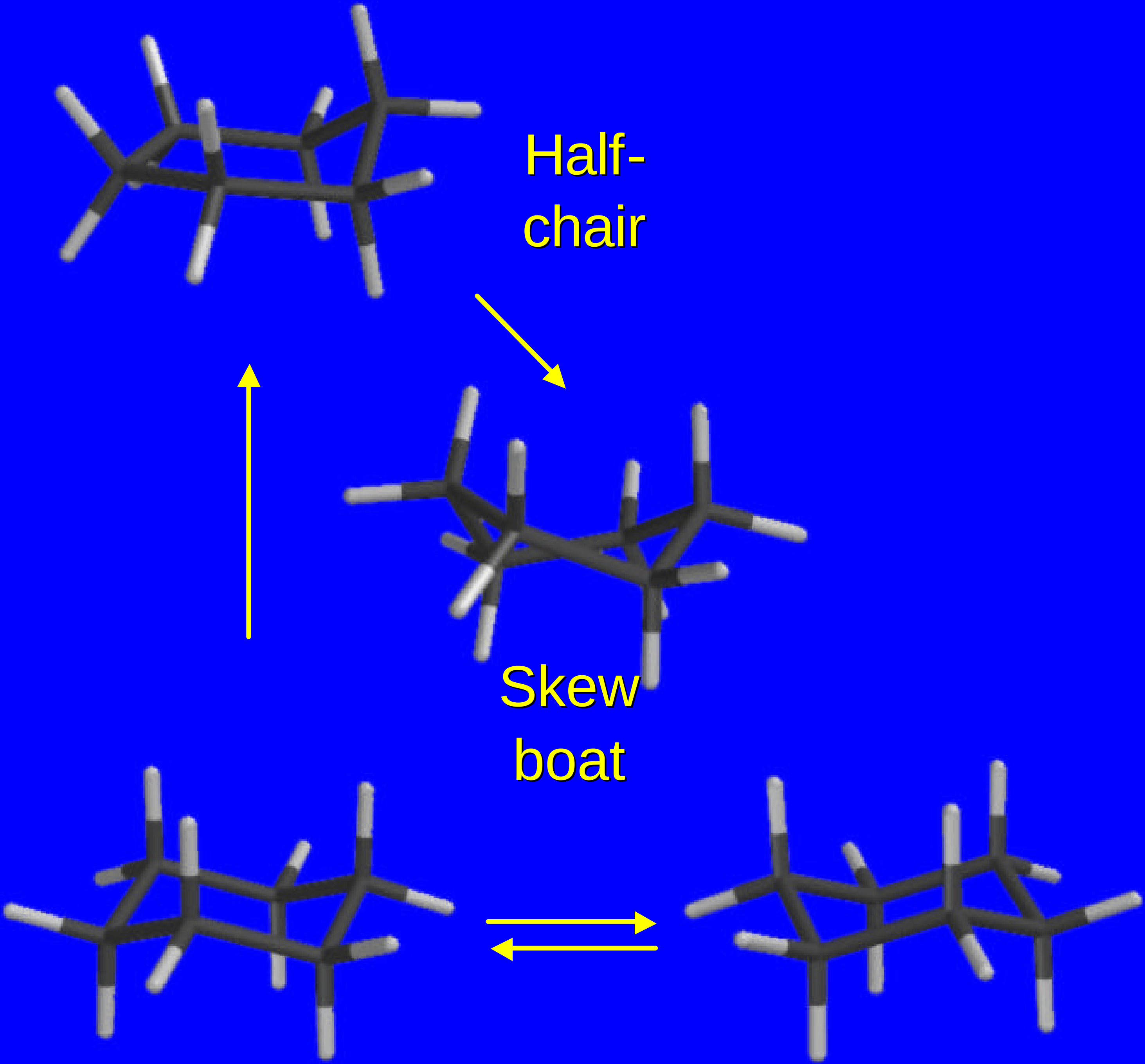
rapid process (activation energy = 45 kJ/mol)

all axial bonds become equatorial and vice versa



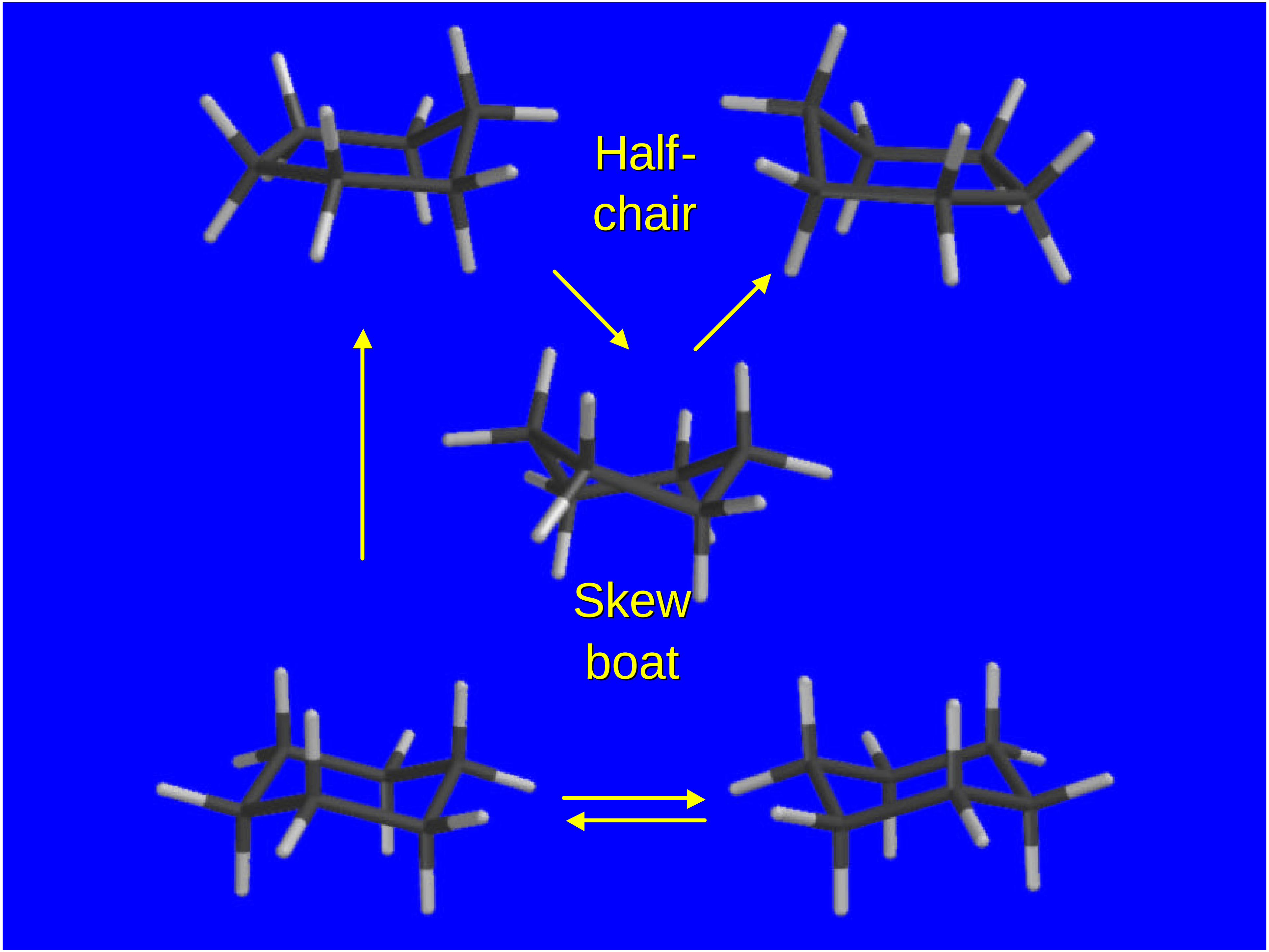


Half-chair



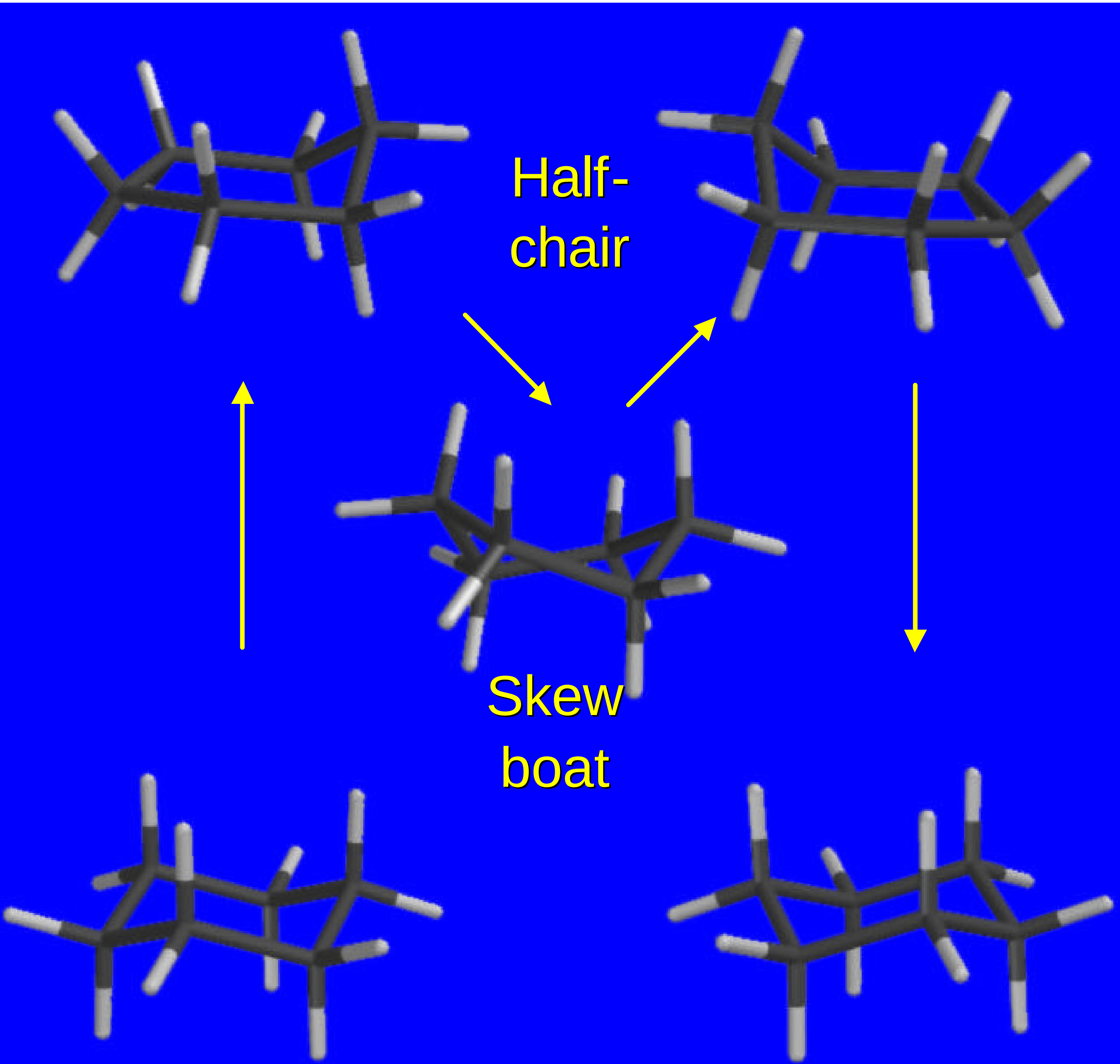
Half-chair

Skew boat



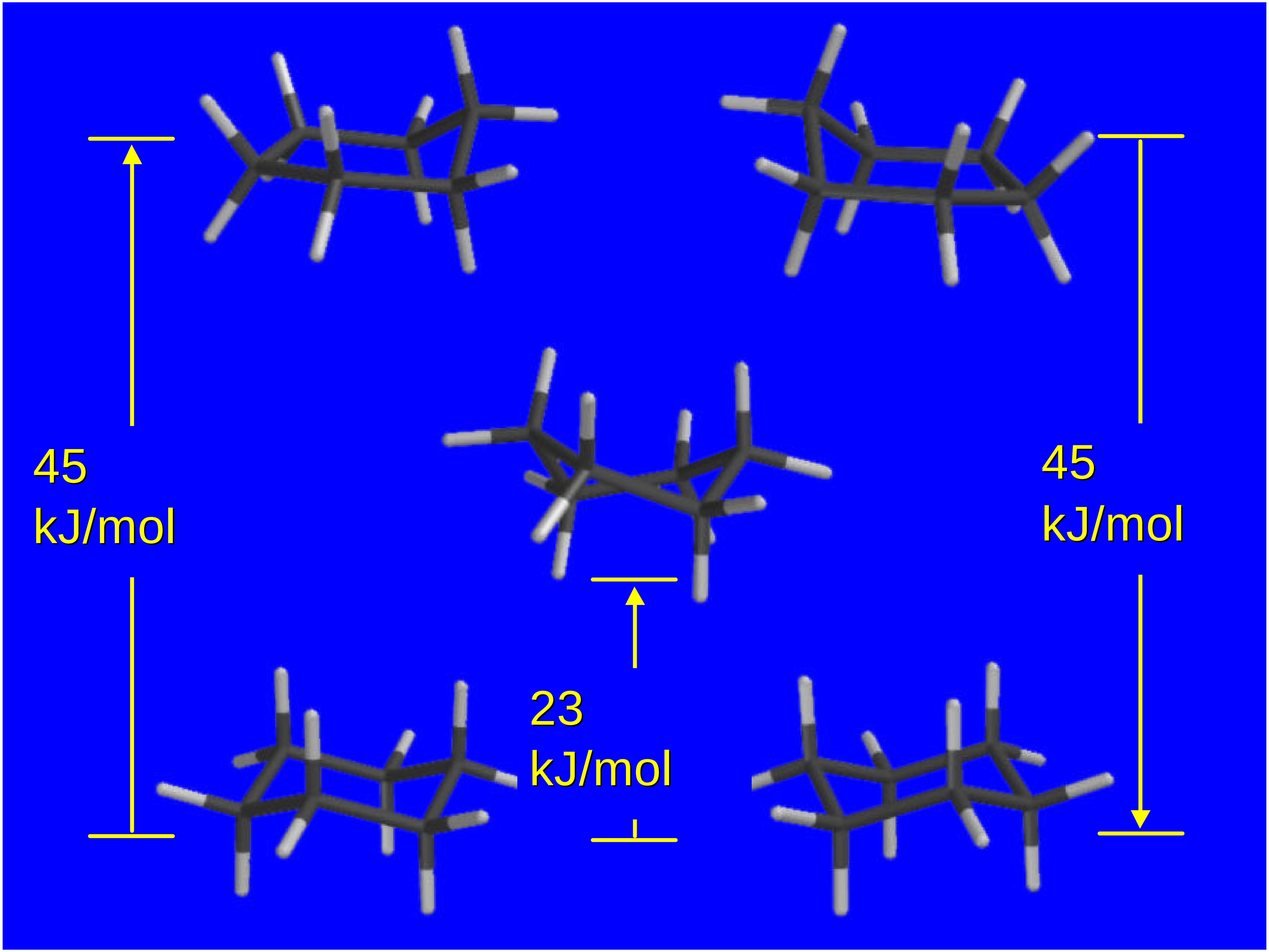
Half-chair

Skew boat



Half-chair

Skew boat



45 kJ/mol

23 kJ/mol

45 kJ/mol

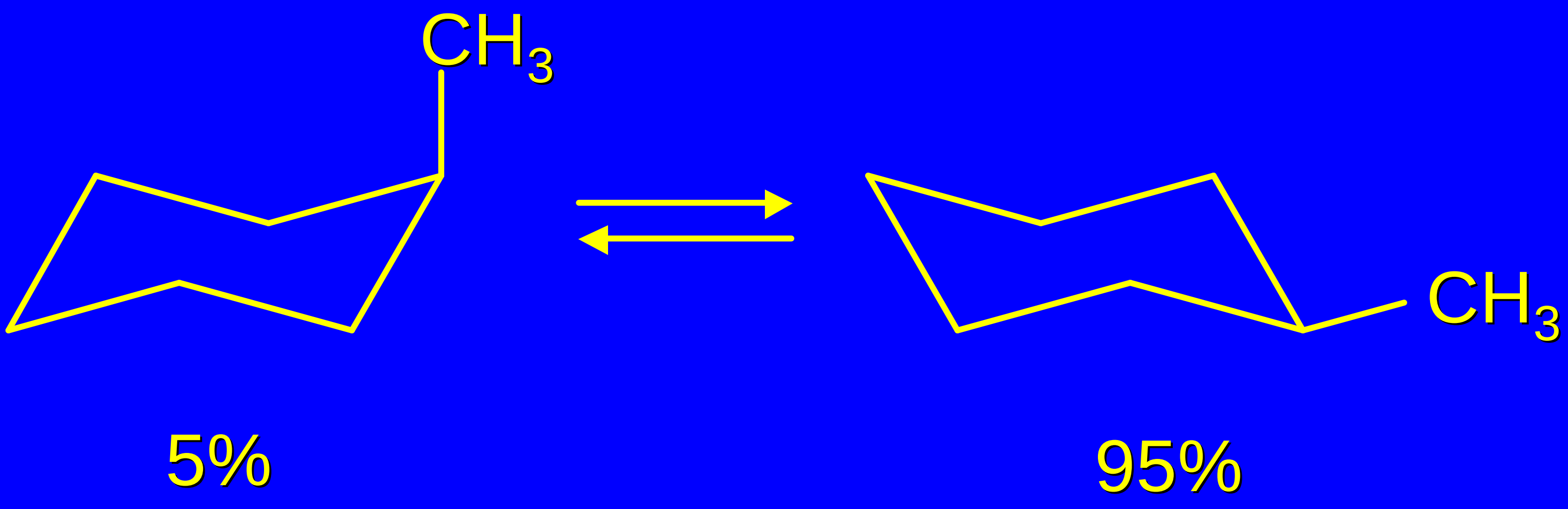
3.8

Conformational Analysis of Monosubstituted Cyclohexanes

most stable conformation is chair

substituent is more stable when equatorial

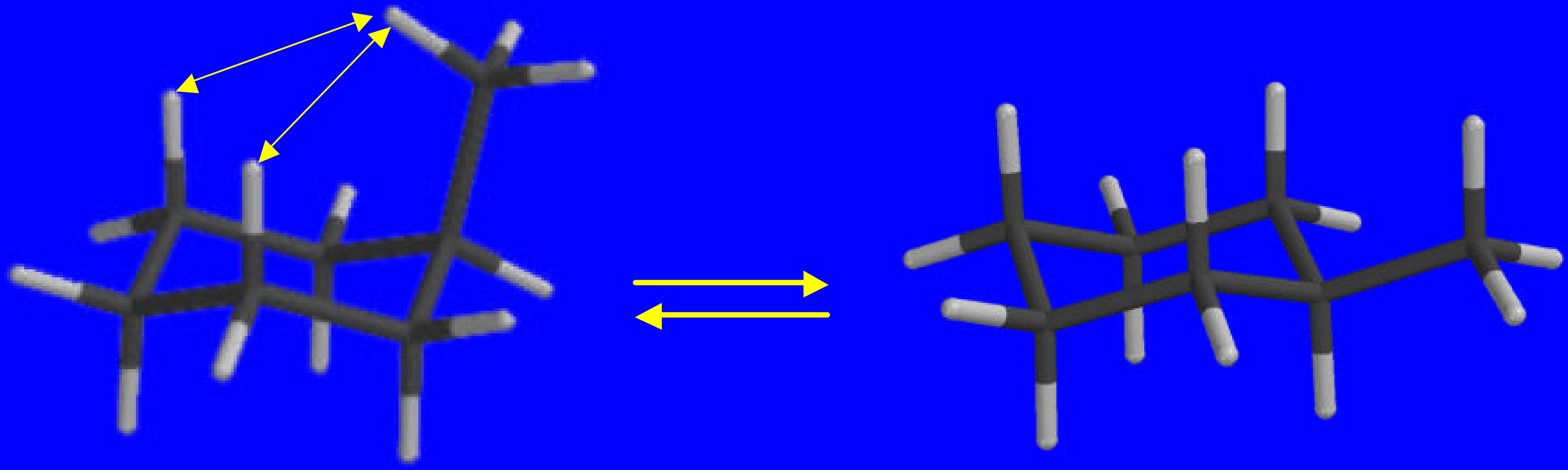
Methylcyclohexane



Chair chair interconversion occurs, but at any instant 95% of the molecules have their methyl group equatorial.

Axial methyl group is more crowded than an equatorial one.

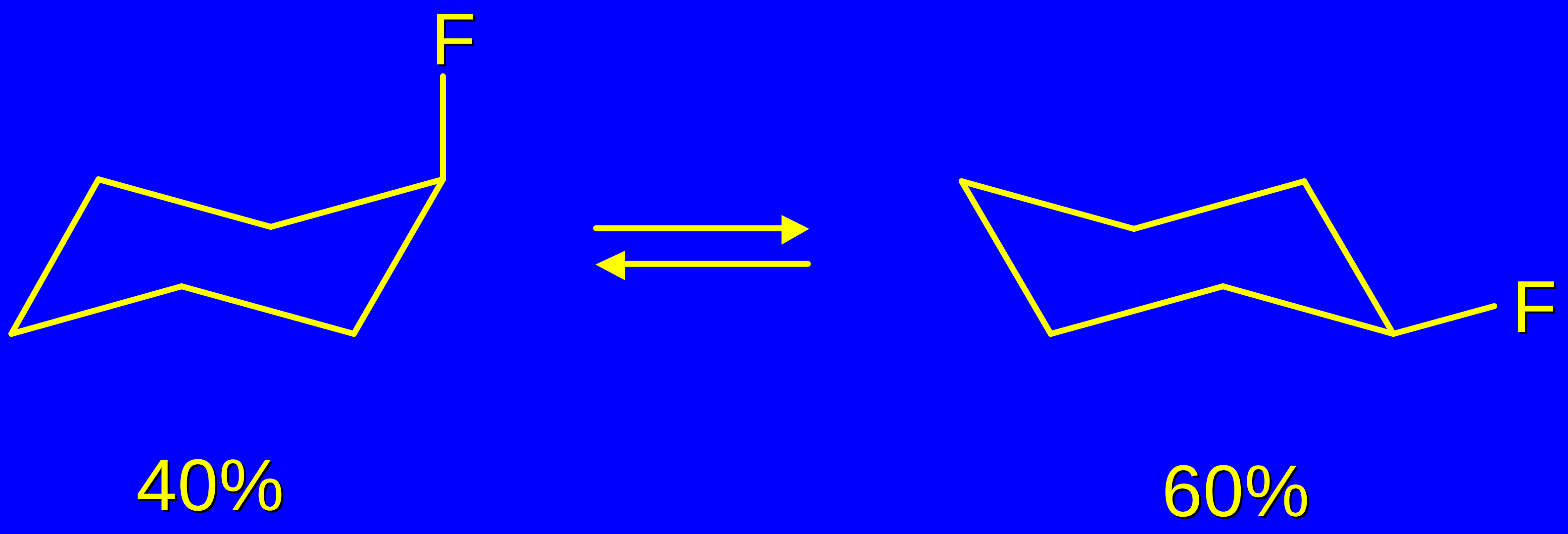
Methylcyclohexane



Source of crowding is close approach to axial hydrogens on same side of ring.

Crowding is called a "1,3-diaxial repulsion" and is a type of van der Waals strain.

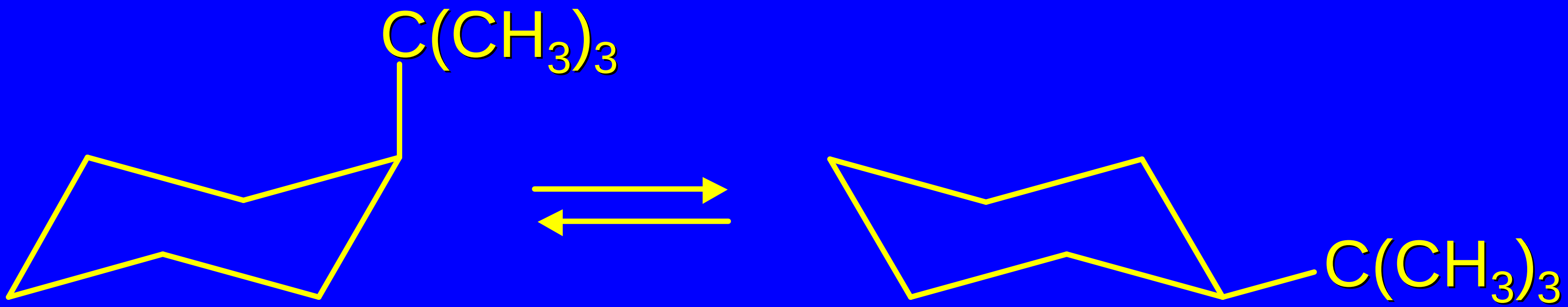
Fluorocyclohexane



Crowding is less pronounced with a "small" substituent such as fluorine.

Size of substituent is related to its branching.

tert-*Butylcyclohexane*



Less than 0.01%

Greater than 99.99%

Crowding is more pronounced with a "bulky" substituent such as *tert*-butyl.

tert-Butyl is highly branched.

tert-*Butylcyclohexane*

van der Waals
strain due to
1,3-diaxial
repulsions