2. Alkanes: The Nature of Organic Compounds

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2.8 Cis-Trans Isomerism in Cycloalkanes

- Cycloalkanes are less flexible than open-chain alkanes
- Much less conformational freedom in cycloalkanes

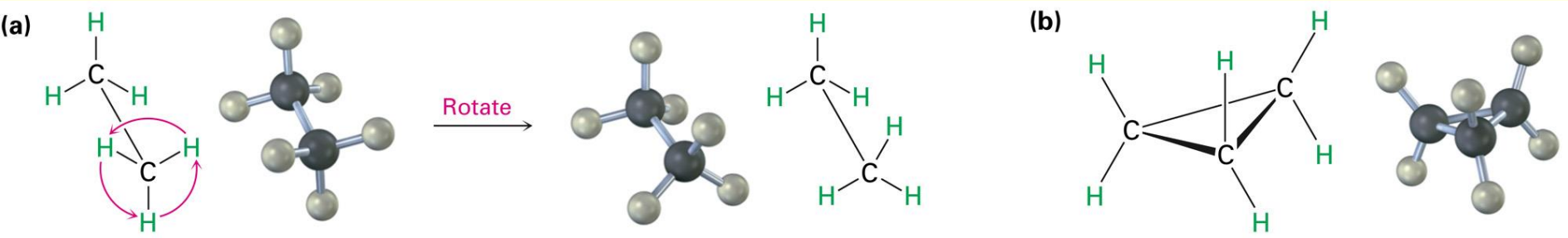
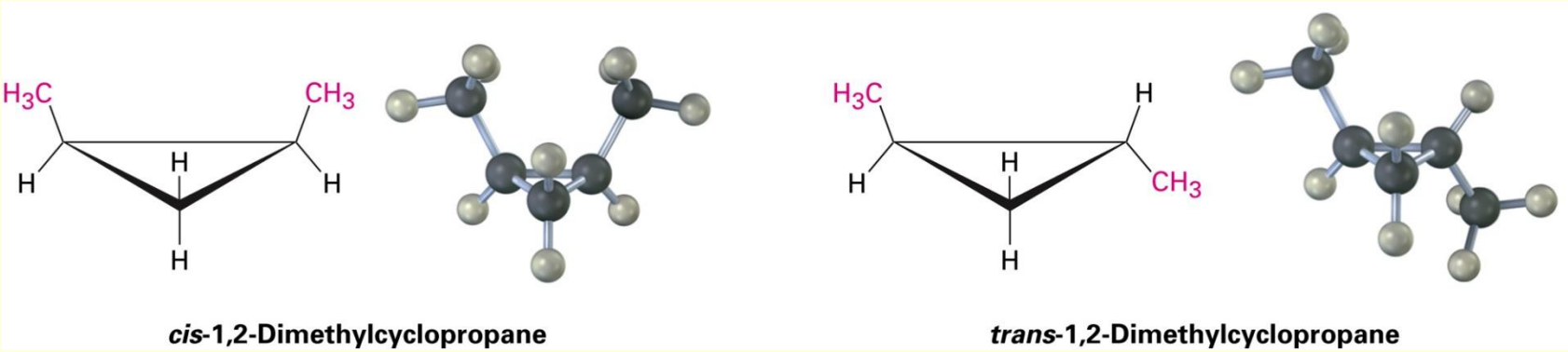


Figure 2.9 **(a)** Rotation occurs around the carbon–carbon bond in ethane, but **(b)** no rotation is possible around the carbon–carbon bonds in cyclopropane without breaking open the ring.

- Because of their cyclic structure, cycloalkanes have 2 faces as viewed edge-on

"top" face "bottom" face

- Therefore, **isomerism** is possible in substituted cycloalkanes
- There are two different 1,2-dimethyl-cyclopropane isomers



cis-1,2-Dimethylcyclopropane *trans*-1,2-Dimethylcyclopropane

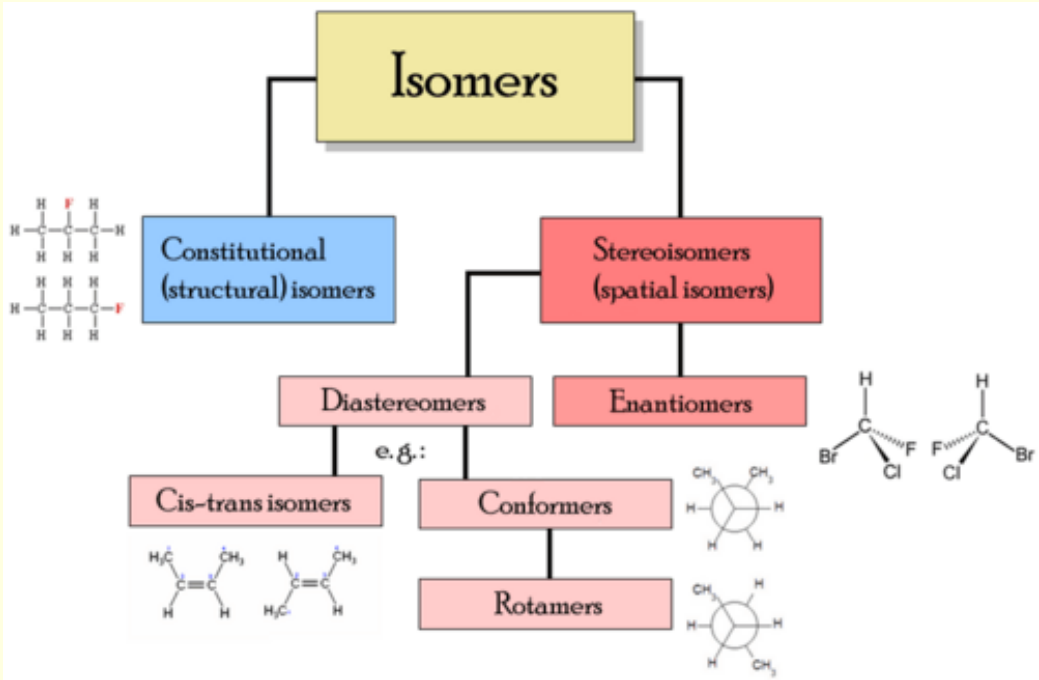
Figure 2.10 There are two different 1,2-dimethylcyclopropane isomers: one with the methyl groups on the **same side of the ring (cis)** and the other with the methyl groups on **opposite sides of the ring (trans**). The two isomers do not **interconvert**.

Cis-trans isomers

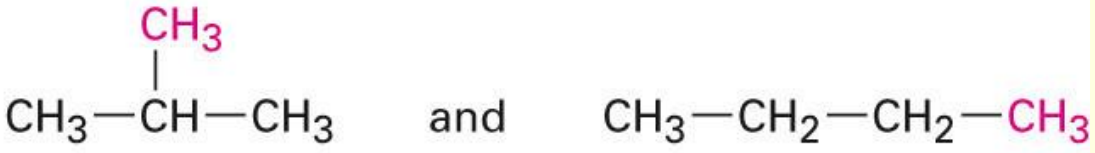
- *Cis*- : on the same side
- *Trans*- : across

Stereoisomerism

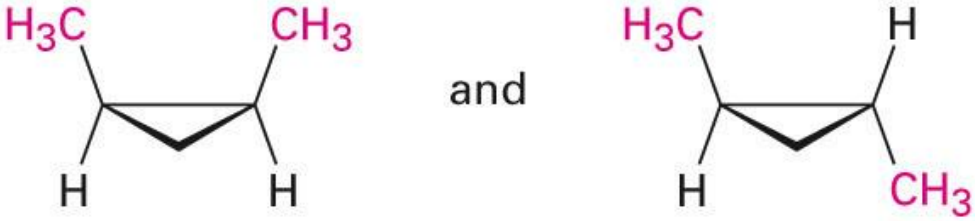
- Compounds which have their atoms **connected in the same order** but differ in **3-D orientation**



Constitutional isomers
(different connections between atoms)



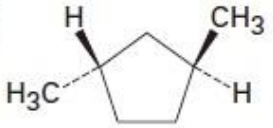
Stereoisomers
(same connections but different three-dimensional geometry)

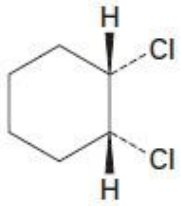


Worked Example 2.6

Naming Cis–Trans Cycloalkane Isomers

Name the following substances, including the *cis*- or *trans*- prefix:

(a) 

(b) 

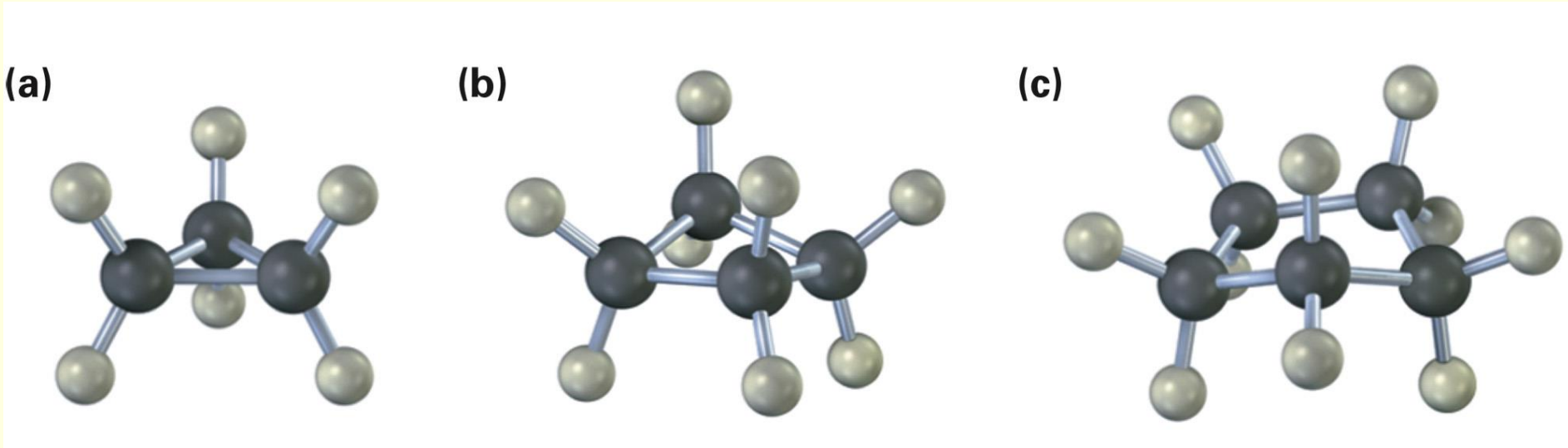
Strategy In these views, the ring is roughly in the plane of the page, a wedged bond protrudes out of the page, and a dashed bond recedes into the page. Two substituents are cis if they are both out of or both into the page, and they are trans if one is out of and one is into the page.

Solution **(a)** *trans*-1,3-Dimethylcyclopentane **(b)** *cis*-1,2-Dichlorocyclohexane

2.9 Conformations of Some Cycloalkanes

Cyclopropane

- 3-membered ring must have planar structure
- Symmetrical with C–C–C bond angles of 60°
- Angle strain

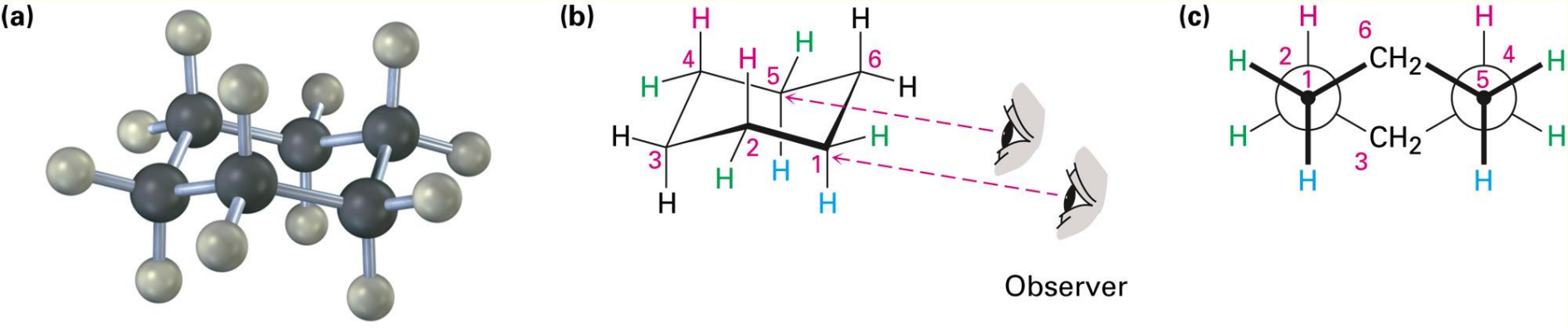


Structures of cyclopropane, cyclobutane and cyclopentane

Cyclopropane is planar, but cyclobutane and cyclopentane are slightly puckered.

Conformations of Cyclohexane

- Substituted cyclohexanes occur widely in nature
- The cyclohexane ring is free of angle strain and torsional strain
- The conformation is has alternating atoms in a common plane and tetrahedral angles between all carbons
- This is called a **chair conformation**



How to Draw Cyclohexane

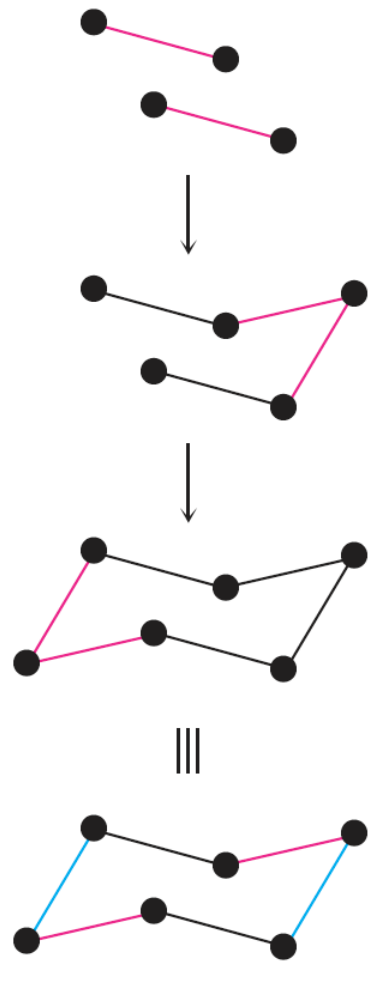
A chair conformation is drawn in three steps.

STEP 1 Draw two **parallel** lines, slanted downward and slightly offset from each other. This means that **four of the cyclohexane carbons lie in a plane**.

STEP 2 Place the **topmost** carbon atom above and to the right of the plane of the other four, and connect the bonds.

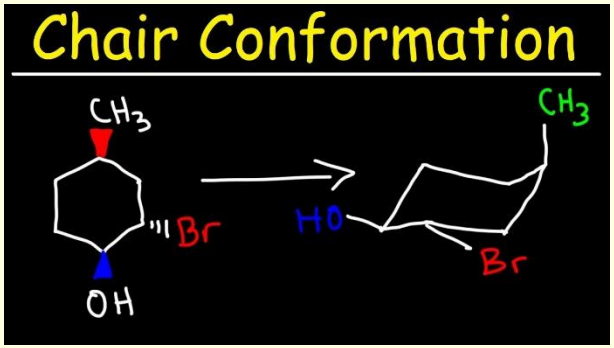
STEP 3 Place the **bottommost** carbon atom below and to the left of the plane of the middle four, and connect the bonds.

Note that the bonds to the **bottommost** carbon atom are **parallel** to the bonds to the **topmost** carbon.



2.10 Axial and Equatorial Bonds in Cyclohexane

- The chair conformation has two kinds of positions for substituents on the ring: ***axial*** positions and ***equatorial*** positions
- Chair cyclohexane has six **axial** hydrogens perpendicular to the ring (parallel to the ring axis) and six **equatorial** hydrogens near the plane of the ring



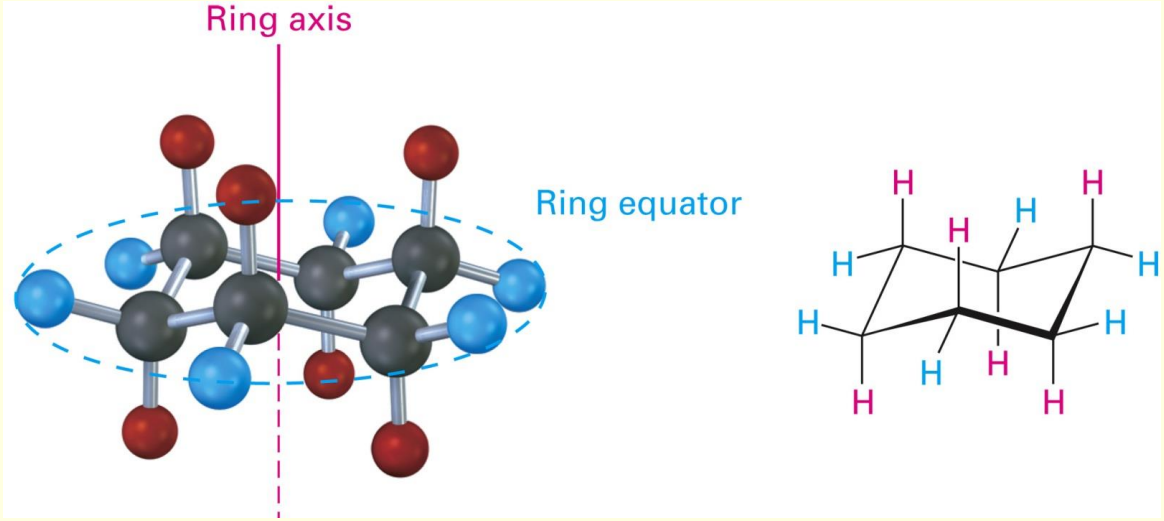
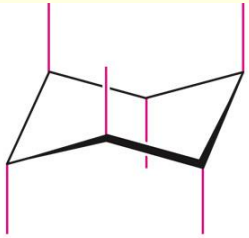


Figure 2.13 Axial (red) and equatorial (blue) positions in chair cyclohexane. The six axial hydrogens are parallel to the ring axis, and the six equatorial hydrogens are in a band around the ring equator.

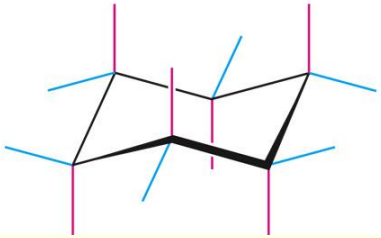
Drawing the Axial and Equatorial Hydrogens

Axial bonds: The six axial bonds, one on each carbon, are parallel and alternate up–down.



Equatorial bonds: The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.

Completed cyclohexane



2.11 Conformational **Mobility** of Cyclohexane

- Chair conformations readily interconvert, resulting in the exchange of axial and equatorial positions by a **ring-flip**

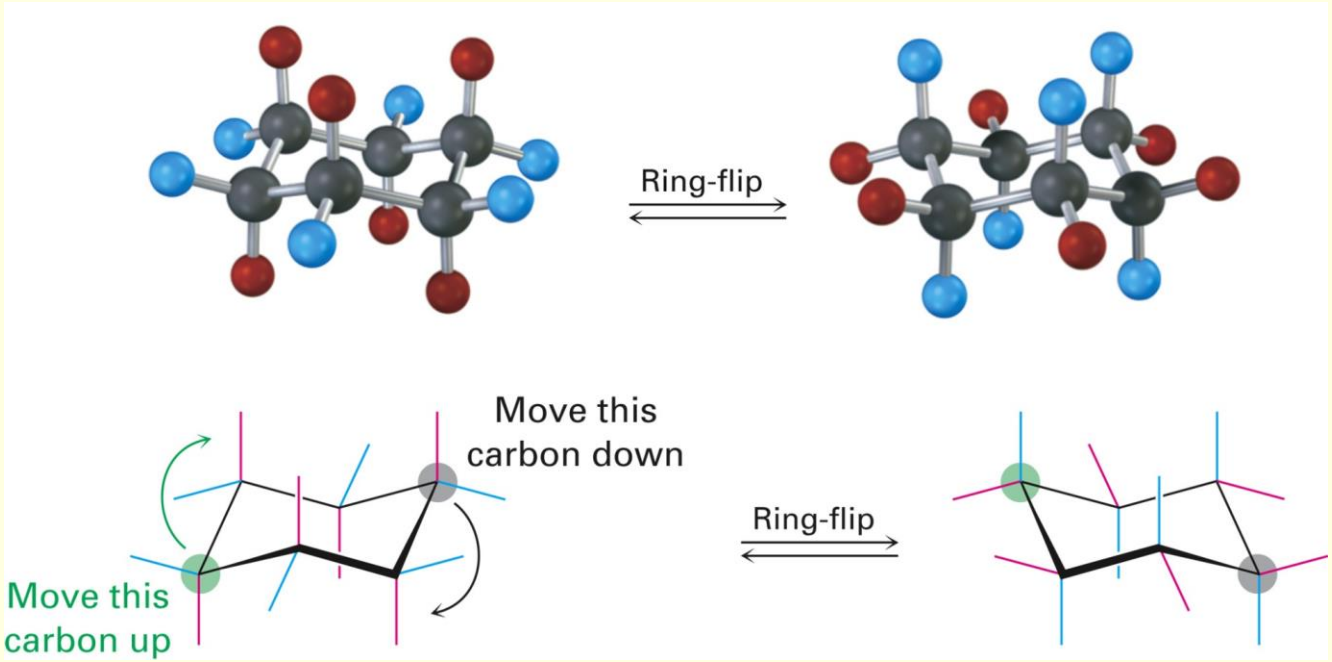


Figure 2.15 A ring-fl ip in chair cyclohexane interconverts axial and equatorial positions. What is axial (red) in the starting structure becomes equatorial in the ring-flipped structure, and what is equatorial (blue) in the starting structure is axial after ring-flip.

Conformations of Monosubstituted Cyclohexanes

- Two conformations of monosubstituted cyclohexane aren't equally stable.
- The **equatorial conformer** of methyl cyclohexane is **more stable** than the axial by 7.6 kJ/mol because of 1,3-diaxial steric interactions in axial conformation.

unfavorable spatial, S*teric* interaction that occurs in the axial conformation between the methyl group on carbon 1 and the axial hydrogen atoms on carbons 3 and 5.

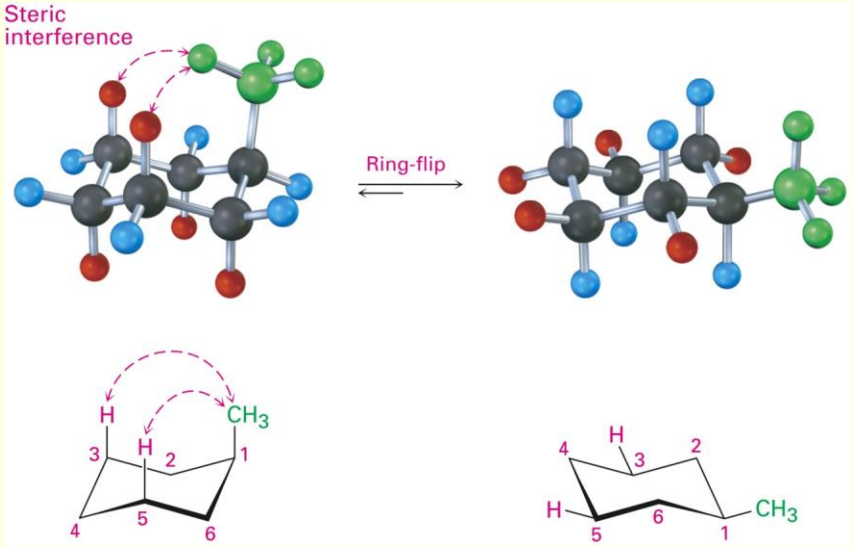


Figure 2.16 Axial versus equatorial methylcyclohexane. The 1,3-diaxial steric interactions in axial methylcyclohexane (easier to see in space-filling models) make the equatorial conformation more stable by 7.6 kJ/mol.

Worked Example 2.7

Drawing Conformations of Substituted Cyclohexanes

Draw 1,1-dimethylcyclohexane in a chair conformation, indicating which methyl group in your drawing is axial and which is equatorial.

Strategy

Draw a chair cyclohexane ring, and then put two methyl groups on the same carbon. The methyl group in the rough plane of the ring is equatorial, and the one directly above or below the ring is axial.

Solution