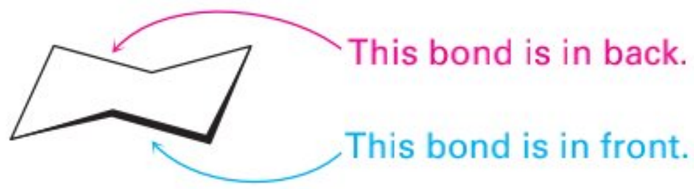
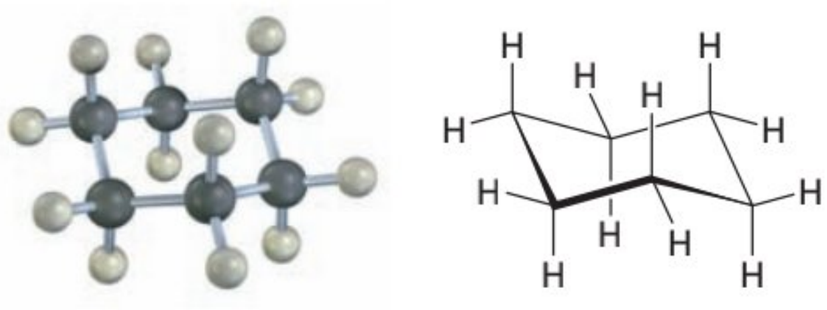
cyclohexane rings drawn in this book will have the front (lower) bond heavily shaded to indicate nearness to the viewer.

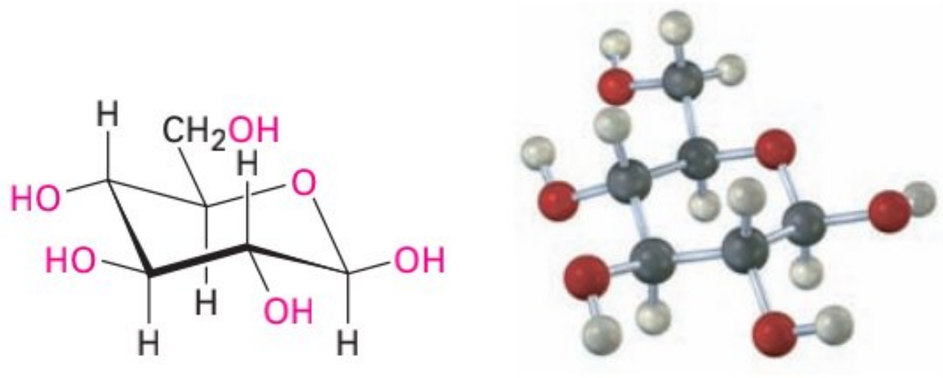


2.10 Axial and Equatorial Bonds in Cyclohexane

The chair conformation of cyclohexane leads to many consequences. We'll see in Section 14.5, for instance, that simple carbohydrates, such as glucose, adopt a conformation based on the cyclohexane chair and that their chemistry is directly affected as a result.



Cyclohexane
(chair conformation)



Glucose
(chair conformation)

Another consequence of the chair conformation is that there are two kinds of positions for substituents on the cyclohexane ring: *axial* positions and *equatorial* positions (Figure 2.13). The six **axial positions** are perpendicular to the ring, parallel to the ring axis, and the six **equatorial positions** are in the rough plane of the ring, around the ring equator. Each carbon atom has one axial and one equatorial position, and each side of the ring has three axial and three equatorial positions in an alternating arrangement.

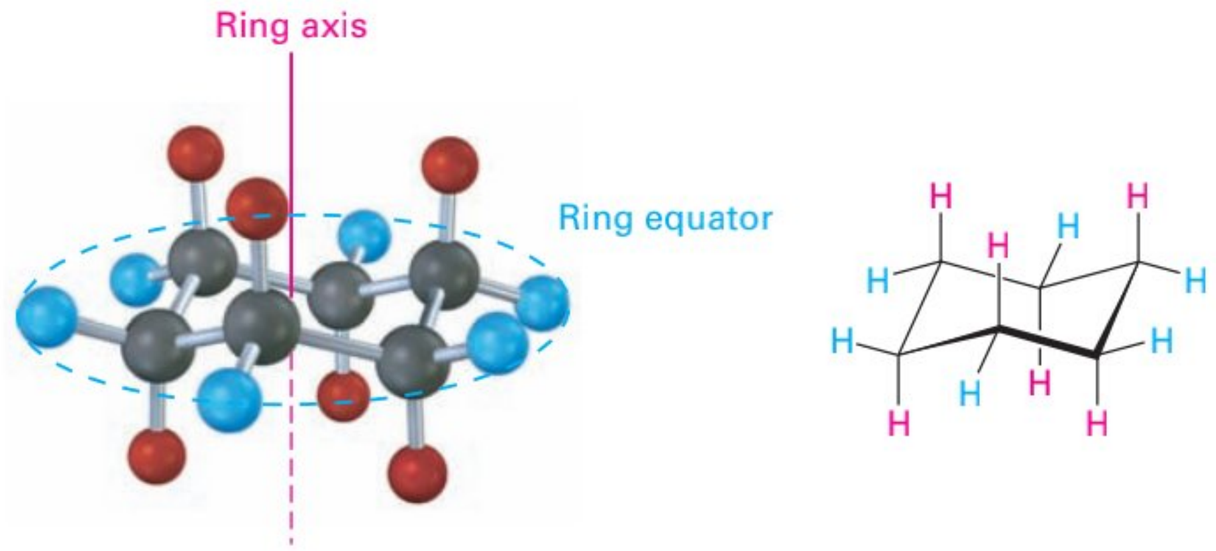


Figure 2.13 Axial (red) and equatorial (blue) positions in chair cyclohexane. The six axial hydrogens are parallel to the ring axis, and the six equatorial hydrogens are in a band around the ring equator.

Note that we haven't used the words *cis* and *trans* in this discussion of cyclohexane conformation. Two hydrogens on the same side of a ring are always cis, regardless of whether they're axial or equatorial and regardless of

whether they're adjacent. Similarly, two hydrogens on opposite sides of the ring are always trans.

Axial and equatorial bonds can be drawn by following the procedure in Figure 2.14.

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

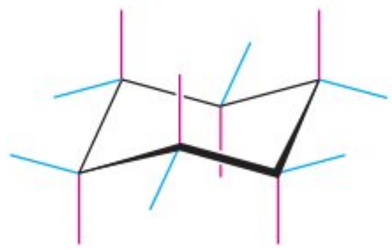


Figure 2.14 A procedure for drawing axial and equatorial bonds in cyclohexane.

Problem 2.24 Draw two chair structures for methylcyclohexane, one with the methyl group axial and one with the methyl group equatorial.

2.11 Conformational Mobility of Cyclohexane

Because chair cyclohexane has two kinds of positions, axial and equatorial, we might expect to find two isomeric forms of a monosubstituted cyclohexane. In fact, we don't. There is only *one* methylcyclohexane, *one* bromocyclohexane, *one* cyclohexanol (hydroxycyclohexane), and so on, because cyclohexane rings are *conformationally mobile* at room temperature. Different chair conformations readily interconvert by a process called a **ring-flip**.

The ring-flip of a chair cyclohexane can be visualized as shown in Figure 2.15 by keeping the middle four carbon atoms in place while folding the two ends in opposite directions. An axial substituent in one chair form becomes an equatorial substituent in the ring-flipped chair form and vice versa. For example, axial methylcyclohexane becomes equatorial methylcyclohexane after ring-flip. Because this interconversion occurs rapidly at room temperature, the individual axial and equatorial isomers can't be isolated.

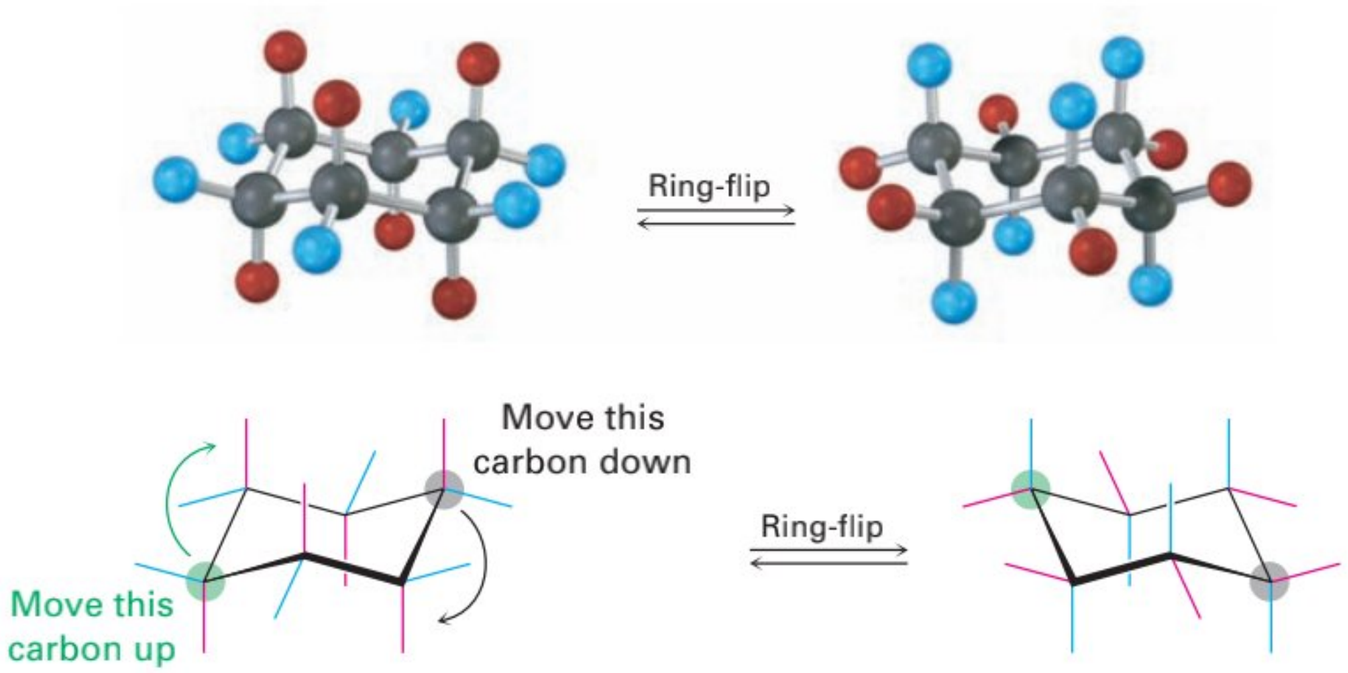


Figure 2.15 A ring-flip in chair cyclohexane interconverts axial and equatorial positions. What is axial (red) in the starting structure becomes equatorial in the ring-flipped structure, and what is equatorial (blue) in the starting structure is axial after ring-flip.

Although axial and equatorial methylcyclohexanes interconvert rapidly, they aren't equally stable. The equatorial conformation is more stable than the axial conformation by 7.6 kJ/mol (1.8 kcal/mol), meaning that about 95% of methylcyclohexane molecules have their methyl group equatorial at any given instant. The energy difference is due to an unfavorable spatial, or *steric,* interaction that occurs in the axial conformation between the methyl group on carbon 1 and the axial hydrogen atoms on carbons 3 and 5. This so-called 1,3-diaxial interaction introduces 7.6 kJ/mol of **steric strain** into the molecule because the axial methyl group and the nearby axial hydrogen are too close together (Figure 2.16).

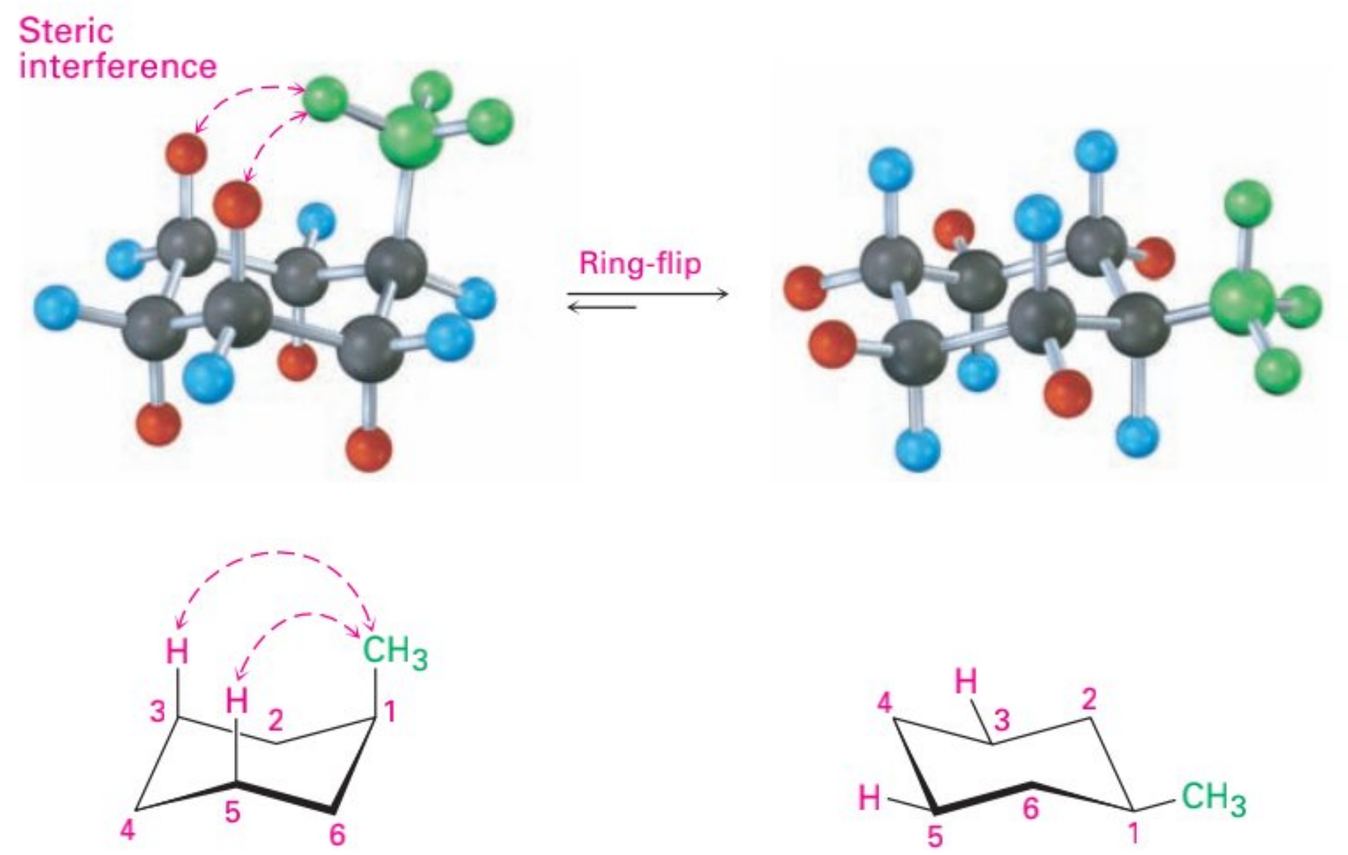


Figure 2.16 Axial versus equatorial methylcyclohexane. The 1,3-diaxial steric interactions in axial methylcyclohexane (easier to see in space-filling models) make the equatorial conformation more stable by 7.6 kJ/mol.

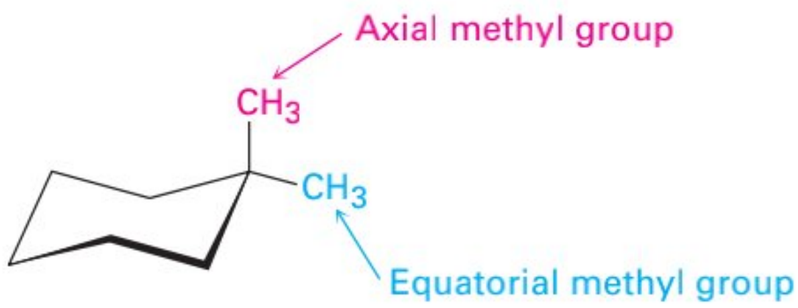
What is true for methylcyclohexane is also true for other monosubstituted cyclohexanes: a substituent is always more stable in an equatorial position than in an axial position. As you might expect, the amount of steric strain increases as the size of the axial substituent group increases.

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



Problem 2.25 Draw two different chair conformations of bromocyclohexane showing all hydrogen atoms. Label all positions as axial or equatorial. Which of the two conformations do you think is more stable?

Problem 2.26 Draw *cis*-1,2-dichlorocyclohexane in a chair conformation, and explain why one chlorine must be axial and one equatorial.

Problem 2.27 Draw *trans*-1,2-dichlorocyclohexane in chair conformation, and explain why both chlorines must be axial or both equatorial.

Problem 2.28 Identify each substituent as axial or equatorial, and tell whether the conformation shown is the more stable or less stable chair form (gray = C, yellow-green = Cl, ivory = H).