Organic Chemistry I

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Organic Chemistry, (9th edition)

By *John McMurry*, Cengage Learning, 2016

Conformations of Cycloalkanes

Cyclopropane is the most strained of all rings, primarily because of the angle strain caused by its 60° C–C–C bond angles. In addition, cyclopropane has considerable torsional strain because the C–H bonds on neighboring carbon atoms are eclipsed.
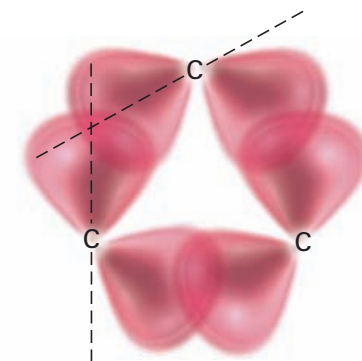
But cyclopropane has **bent bonds**.

In an unstrained alkane, maximum bonding is achieved when two atoms have their overlapping orbitals pointing directly toward each other. In cyclopropane, the orbitals overlap at a slight angle.

The result is that cyclopropane bonds are weaker and more reactive than typical alkane bonds—255 kJ/mol (61 kcal/mol) for a C–C bond in cyclopropane versus 370 kJ/mol (88 kcal/mol) for a C–C bond in open-chain propane.

(a)

(b)

Eclipsed

Eclipsed

109°
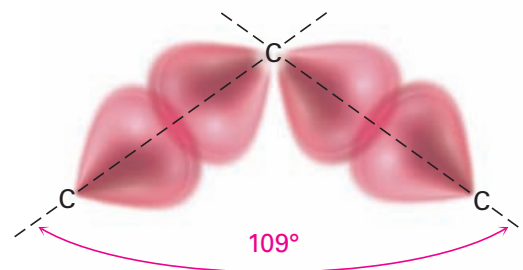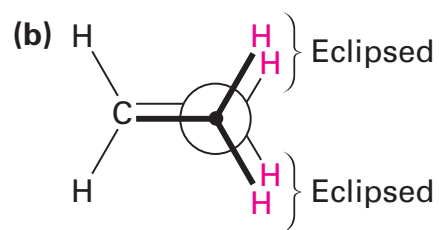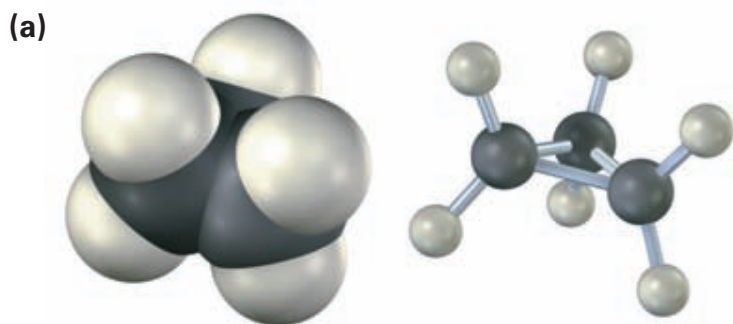
Typical alkane C–C bonds

Typical bent cyclopropane C–C bonds

Cyclobutane has less angle strain than cyclopropane but has more torsional strain because of its larger number of ring hydrogens.

As a result, the total strain for the two compounds is nearly the same—110 kJ/mol (26.4 kcal/mol) for cyclobutane versus 115 kJ/mol (27.5 kcal/mol) for cyclopropane.
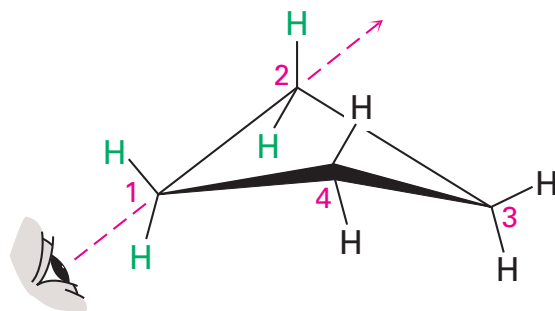
Cyclobutane is not quite flat but is slightly bent so that one carbon atom lies about 25° above the plane of the other three.

The effect of this slight bend is to *increase* **angle strain** but to *decrease* **torsional strain**, until a minimum-energy balance between the two opposing effects is achieved.
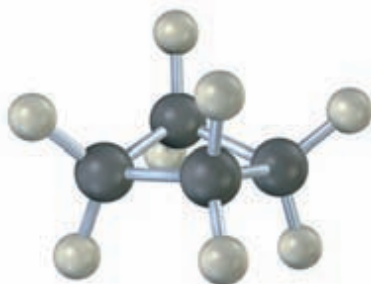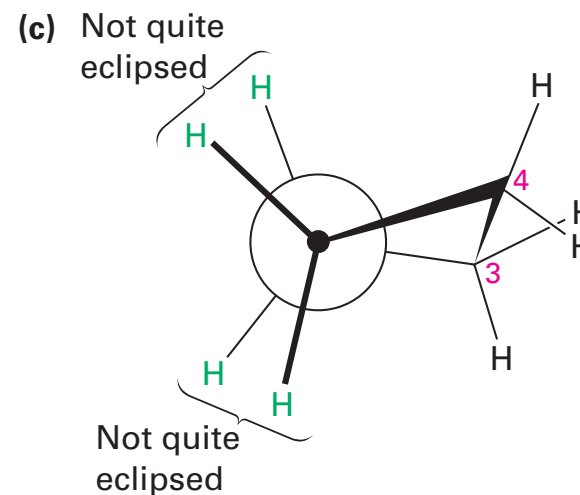
Cyclopentane was predicted by Baeyer to be nearly strain-free, but it actually has a total strain energy of 26 kJ/mol (6.2 kcal/mol).

Although planar cyclopentane has practically no angle strain, it has a large torsional strain.

Cyclopentane therefore twists to adopt a puckered, nonplanar conformation that strikes a balance between increased angle strain and decreased torsional strain.

Four of the cyclopentane carbon atoms are in approximately the same plane, with the fifth carbon atom bent out of the plane. Most of the hydrogens are nearly staggered with respect to their neighbors.

(a)

(b)

Observer

(c)
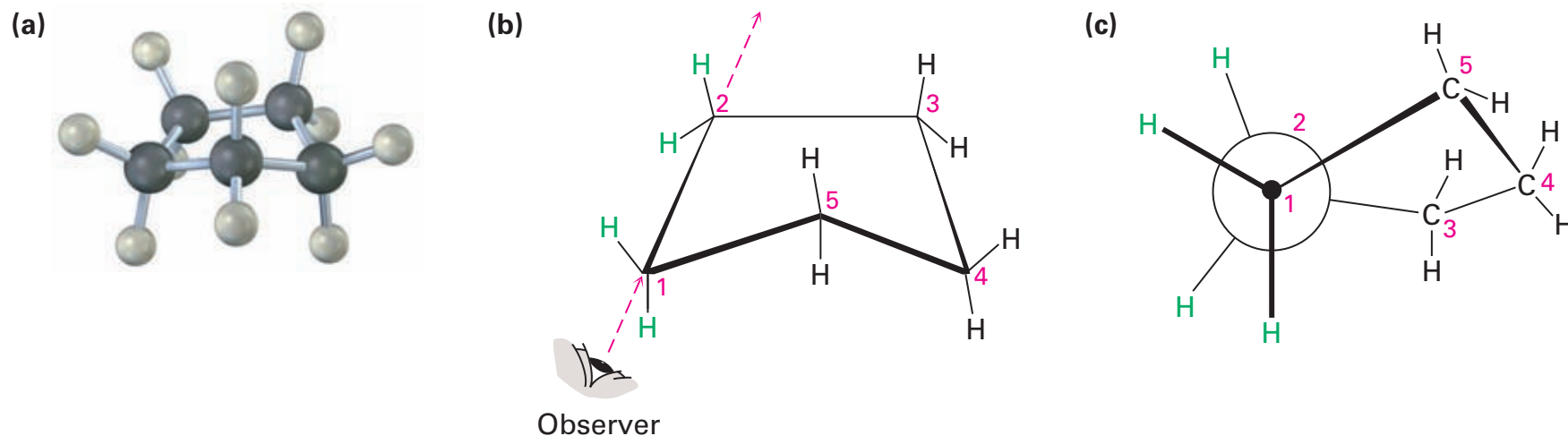
Cyclohexane adopts a strain-free, three-dimensional shape that is called a **chair conformation** because of its similarity to a lounge chair, with a back, seat, and footrest.

Chair cyclohexane has neither angle strain nor torsional strain—all C–C–C bond angles are near the 109° tetrahedral value, and all neighboring C–H bonds are staggered.

Observer
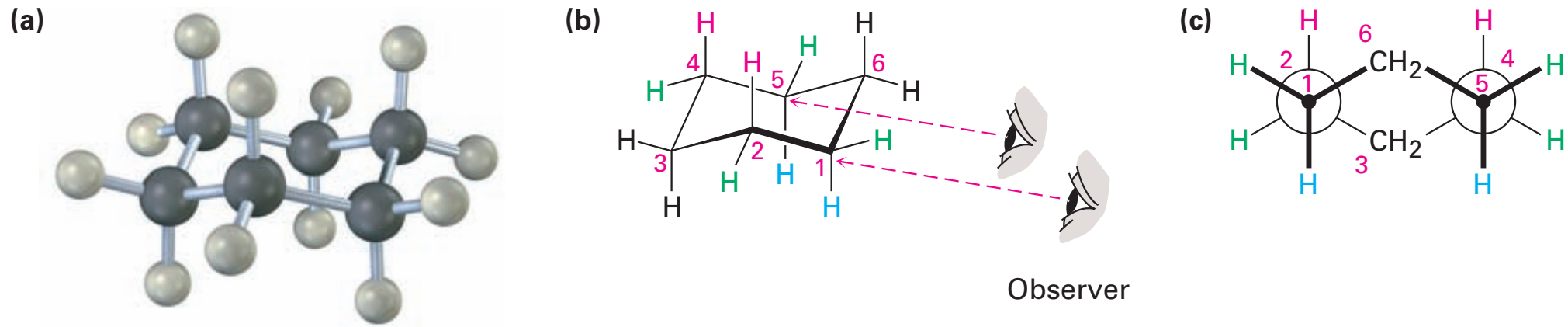
In addition to the chair conformation of cyclohexane, there is an alternative conformation of cyclohexane that bears a slight resemblance to a boat.

Boat cyclohexane has no angle strain but has a large number of eclipsing interactions that make it less stable than chair cyclohexane.

A "twist" on this alternative can be found in **twist-boat conformation,** which is also nearly free of angle strain. It has both steric strain and torsional strain and is about 23 kJ/mol (5.5 kcal/mol) higher in energy than the chair conformation.
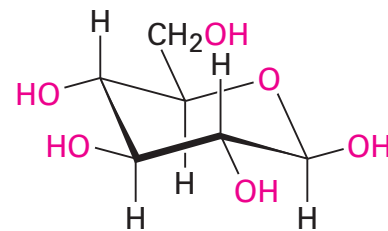
Steric strain
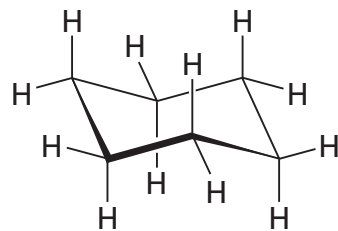
H ↔ H
H ↔ H } **Torsional strain**
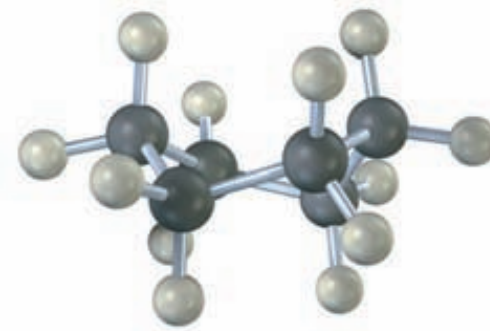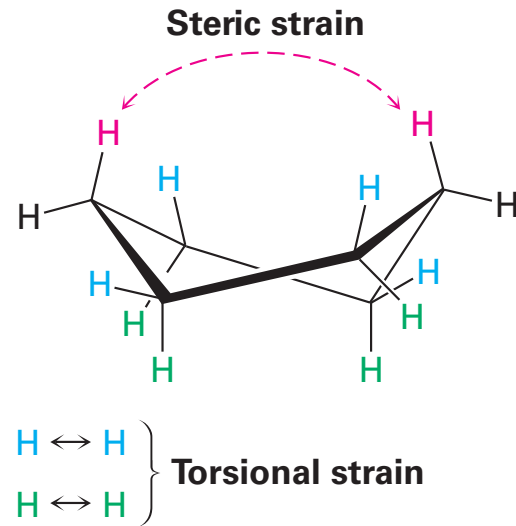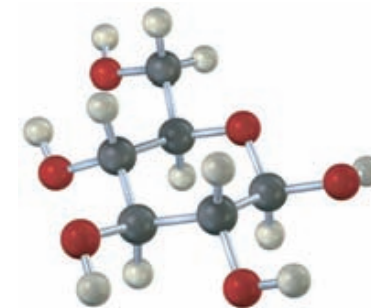
**Twist-boat cyclohexane
(23 kJ/mol strain)**

Simple carbohydrates, such as glucose, adopt a conformation based on the cyclohexane chair and that their chemistry is directly affected as a result.
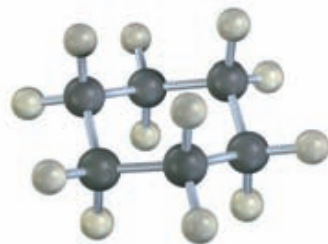
**Cyclohexane
(chair conformation)**

**Glucose
(chair conformation)**

There are two kinds of positions for substituents on the cyclohexane ring: *axial* positions and *equatorial* positions. 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 in chair cyclohexane has one axial and one equatorial hydrogen. Furthermore, each face of the ring has three axial and three equatorial hydrogens in an alternating arrangement.

For example, if the top face of the ring has axial hydrogens on carbons 1, 3, and 5, then it has equatorial hydrogens on carbons 2, 4, and 6. The reverse is true for the bottom face: carbons 1, 3, and 5 have equatorial hydrogens, but carbons 2, 4, and 6 have axial hydrogens.
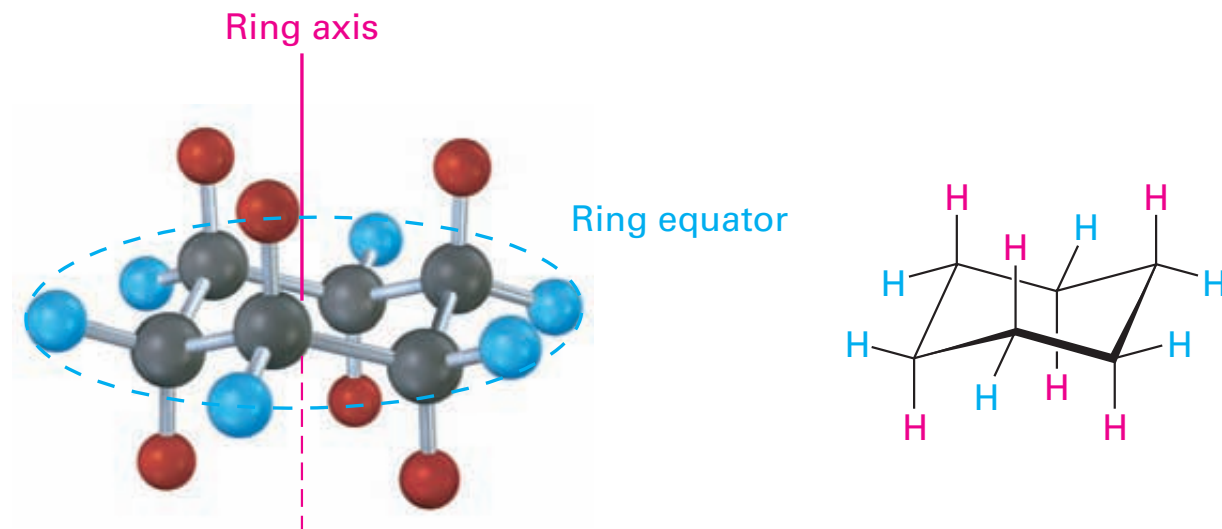
Two hydrogens on the same face of the ring are always *cis*, regardless of whether they're axial or equatorial and regardless of whether they're adjacent.

Similarly, two hydrogens on opposite faces of the ring are always *trans*.
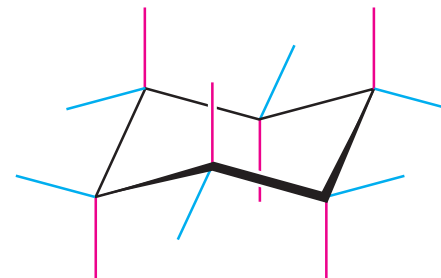
Axial bonds: The six axial bonds, one on each carbon, are parallel and alternate up–down.
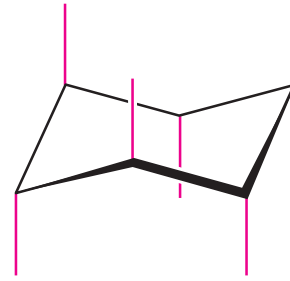
Equatorial bonds: The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.

Completed cyclohexane

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, and so on, because cyclohexane rings are *conformationally mobile* at room temperature.

Different chair conformations readily interconvert, exchanging axial and equatorial positions. This interconversion, usually called a **ring-flip**.
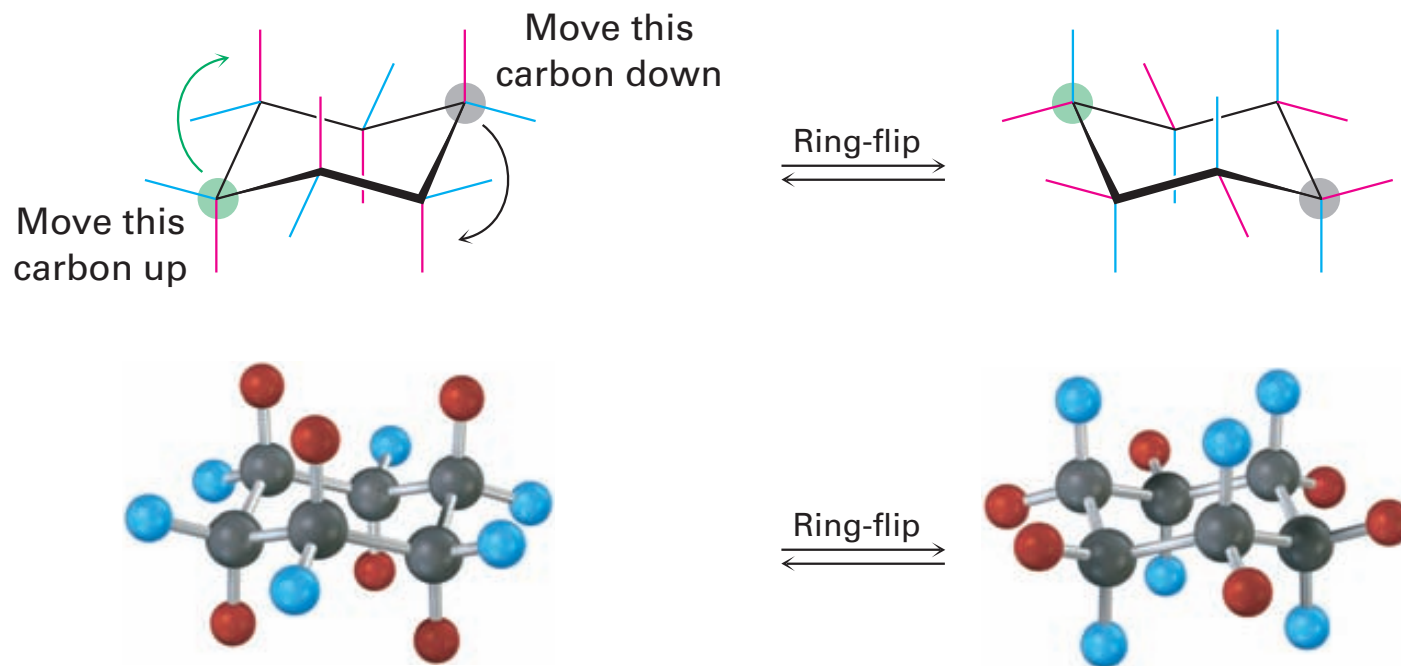
A chair cyclohexane can be ring-flipped by keeping the middle four carbon atoms in place while folding the two end carbons in opposite directions.

Therefore, an axial substituent in one chair form becomes an equatorial substituent in the ring-flipped chair form and vice versa. For example, axial bromocyclohexane becomes equatorial bromocyclohexane after a ring-flip.

Since the energy barrier to chair–chair interconversion is only about 45 kJ/mol (10.8 kcal/mol), the process is rapid at room temperature.

Ring-flip

Axial bromocyclohexane   **Equatorial bromocyclohexane**
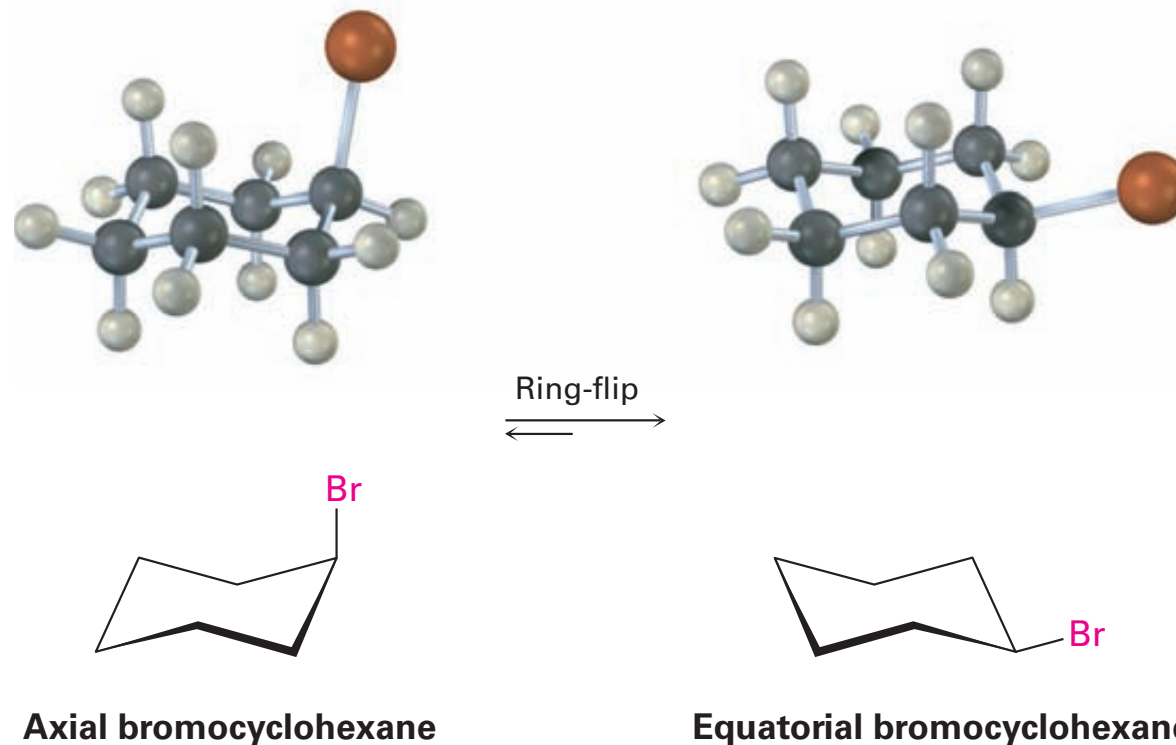
Cyclohexane rings flip rapidly between chair conformations at room temperature, the two conformations of a monosubstituted cyclohexane aren't equally stable. In methylcyclohexane, the equatorial conformation (95%) is more stable than the axial conformation (5%) by 7.6 kJ/mol (1.8 kcal/mol).

The energy difference between axial and equatorial conformations is due to steric strain caused by **1,3-diaxial interactions**. The axial methyl group on C1 is too close to the axial hydrogens three carbons away on C3 and C5, resulting in 7.6 kJ/mol of steric strain.