

Organic Chemistry I

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STRUCTURAL AND PHYSICAL PROPERTIES OF ALKANES

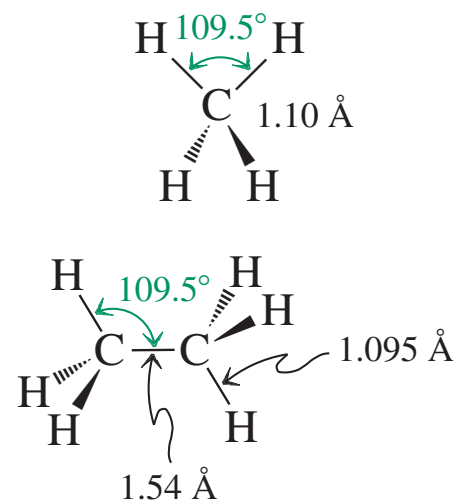
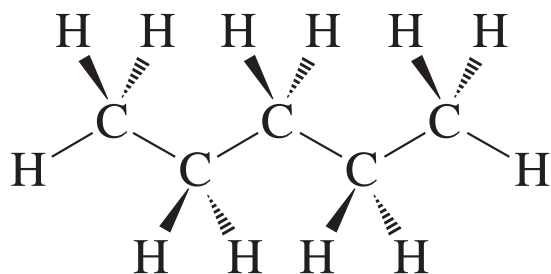
The common structural feature of all alkanes is the carbon chain.

Alkanes exhibit regular molecular structures and properties

The carbon atoms are tetrahedral, with bond angles close to 109° and with regular C–H ($< 1.10 \text{ \AA}$) and C–C ($< 1.54 \text{ \AA}$) bond lengths.

Alkane chains often adopt the zigzag patterns used in bond-line notation. To depict three-dimensional structures, we shall make use of the hashed-wedged line notation.

The main chain and a hydrogen at each end are drawn in the plane of the page.

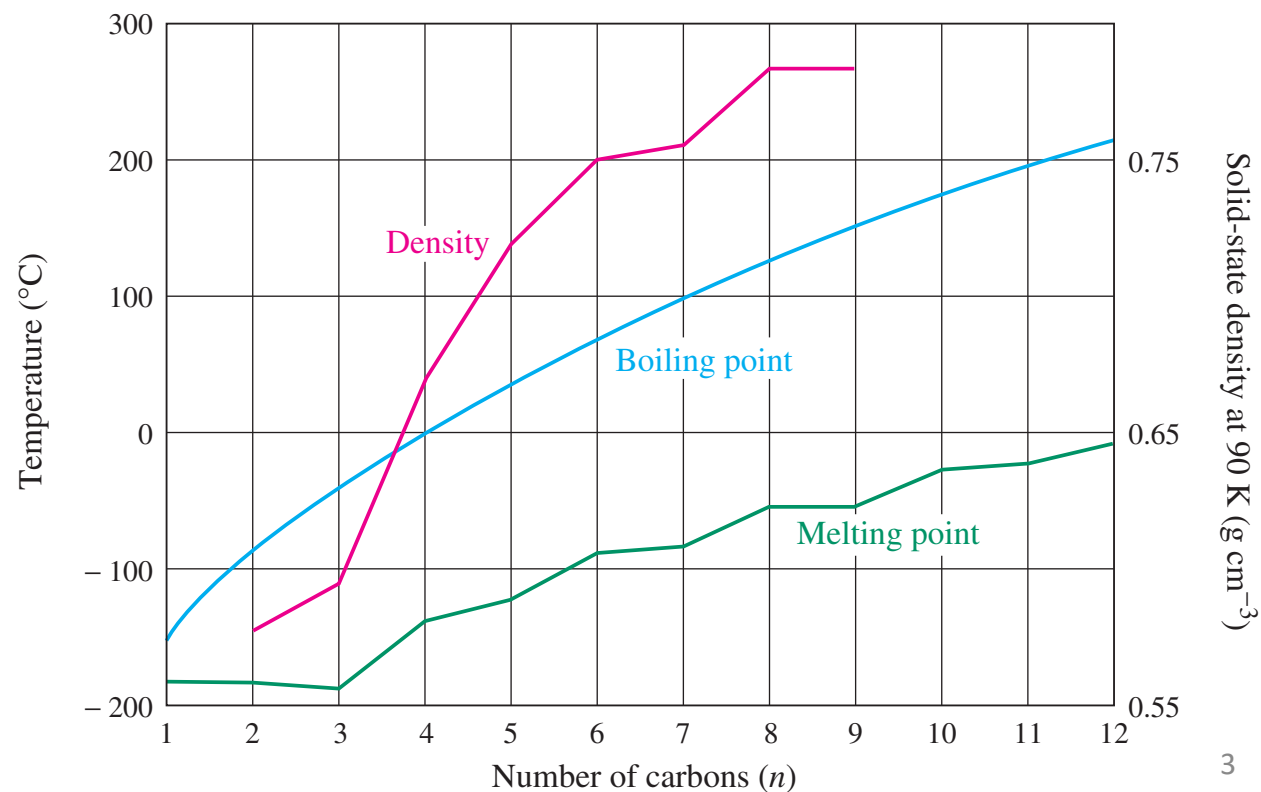


The regularity in alkane structures suggests that their physical constants would follow predictable trends. Indeed, inspection of the data reveals regular incremental increases along the homologous series.

For example, at room temperature (25 °C), the lower homologs of the alkanes are gases or colorless liquids, the higher homologs are waxy solids. From pentane to pentadecane, each additional CH₂ group causes a 20–30 °C increase in boiling point.

In alkanes, melting points rise with increasing molecular size due to greater London attractions.

Branched alkanes have weaker attractions result in lower melting and boiling points.



Attractive forces between molecules govern the physical properties of alkanes

Such trends exist because of **intermolecular** or **van der Waals forces**. Molecules exert several types of attractive forces on each other, causing them to aggregate into organized arrangements as solids and liquids. Most solid substances exist as highly ordered crystals.

Ionic compounds, such as salts, are rigidly held in a crystal lattice, mainly by strong Coulomb forces.

Nonionic but *polar* molecules, such as chloromethane (CH_3Cl), are attracted by weaker dipole–dipole interactions, also of coulombic origin.

The *nonpolar* alkanes attract each other by **London forces**, which are due to **electron correlation**. When one alkane molecule approaches another, repulsion of the electrons in one molecule by those in the other results in correlation of their movement.

Electron motion causes temporary bond polarization in one molecule; correlated electron motion in the bonds of the other induces polarization in the opposite direction, resulting in attraction between the molecules.

ROTATION ABOUT SINGLE BONDS: CONFORMATIONS

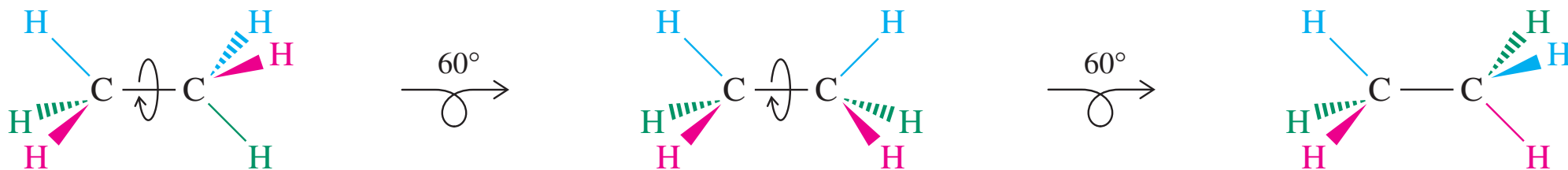
How the forces present *within* molecules (i.e., intramolecular forces) make some geometric arrangements of the atoms energetically more favorable than others?

Rotation interconverts the conformations of ethane

If we build a molecular model of ethane, we can see that the two methyl groups are readily rotated with respect to each other. The energy required to move the hydrogen atoms past each other, the **barrier to rotation**, is only $2.9 \text{ kcal mol}^{-1}$ (12.1 kJ mol^{-1}). This value turns out to be so low that chemists speak of “free rotation” of the methyl groups.

In general, *there is free rotation about all single bonds* at room temperature.

The rotational movement in ethane by the use of hashed-wedged line structures:

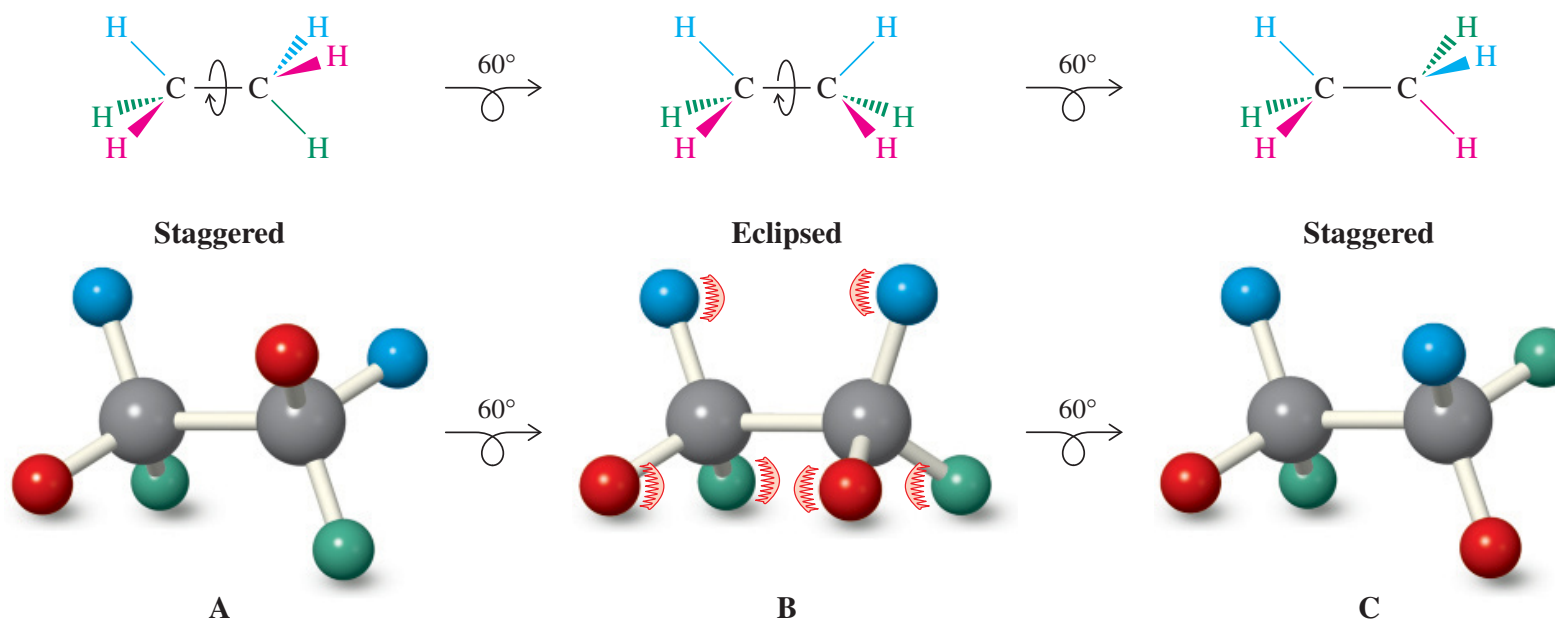


There are two extreme ways of drawing ethane: **staggered** and **eclipsed**.

A 60° turn converts the staggered form into the eclipsed arrangement.

Many forms of ethane created by such rotations, called **conformations** (also called **conformers**). All of them rapidly interconvert at room temperature.

The study of their thermodynamic and kinetic behavior is **conformational analysis**.

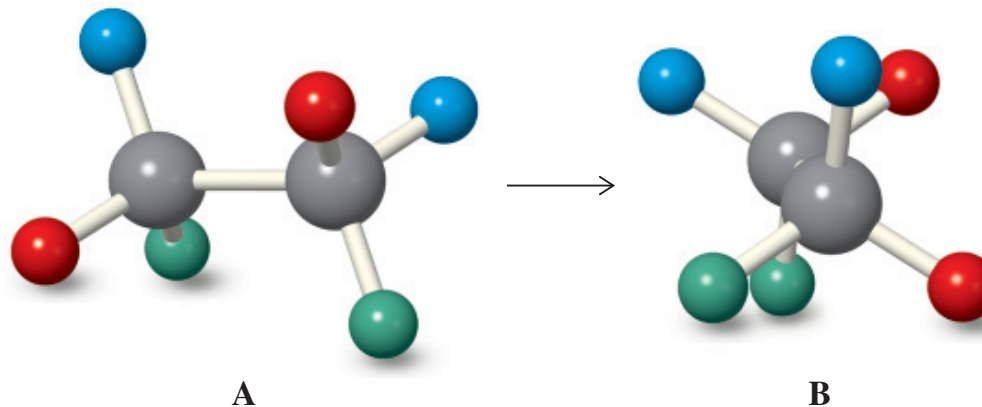
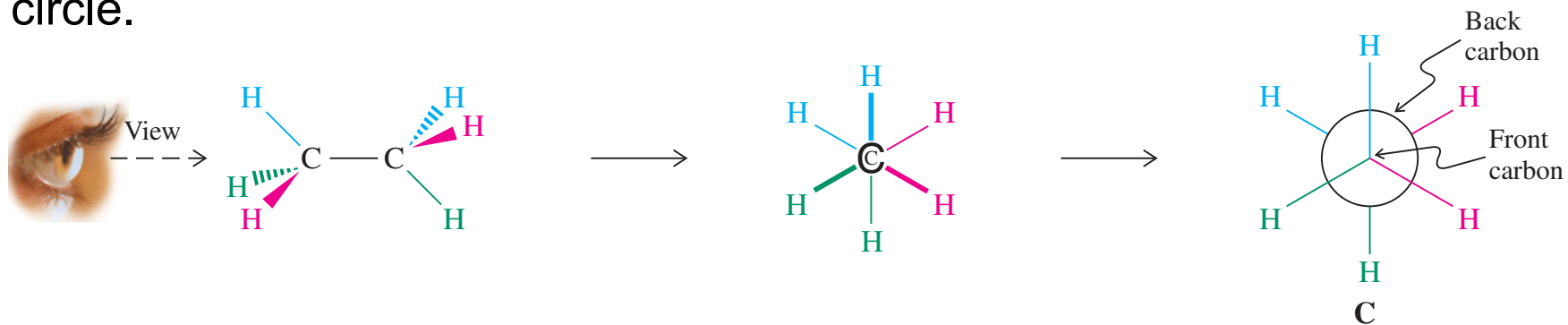


Newman projection

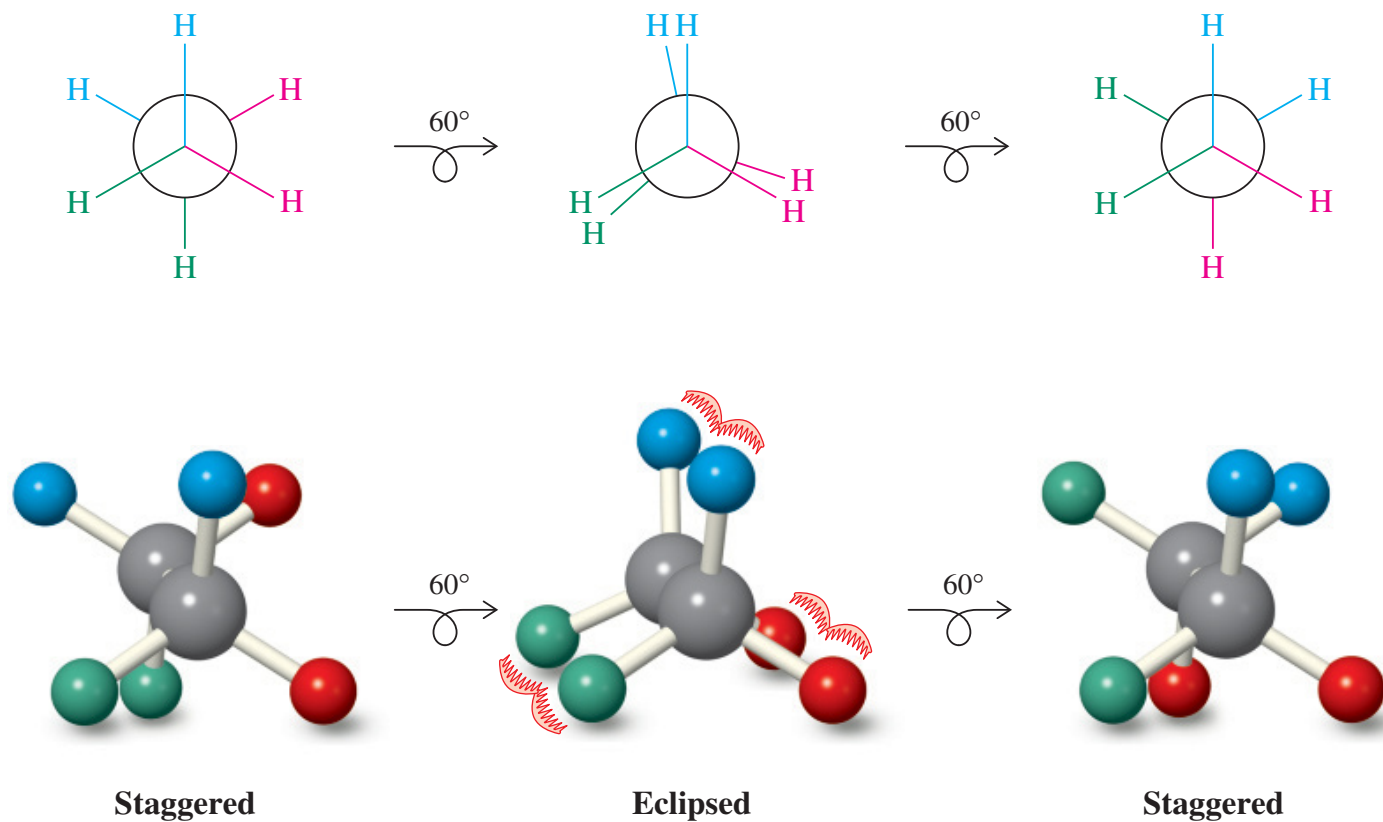
Viewing the molecule along the C–C axis. The front carbon obscures the back carbon, but the bonds emerging from both are clearly seen.

The front carbon is depicted as the point of juncture of the three bonds attached to.

The back carbon is represented by a circle. The bonds to this carbon project from the outer edge of the circle.



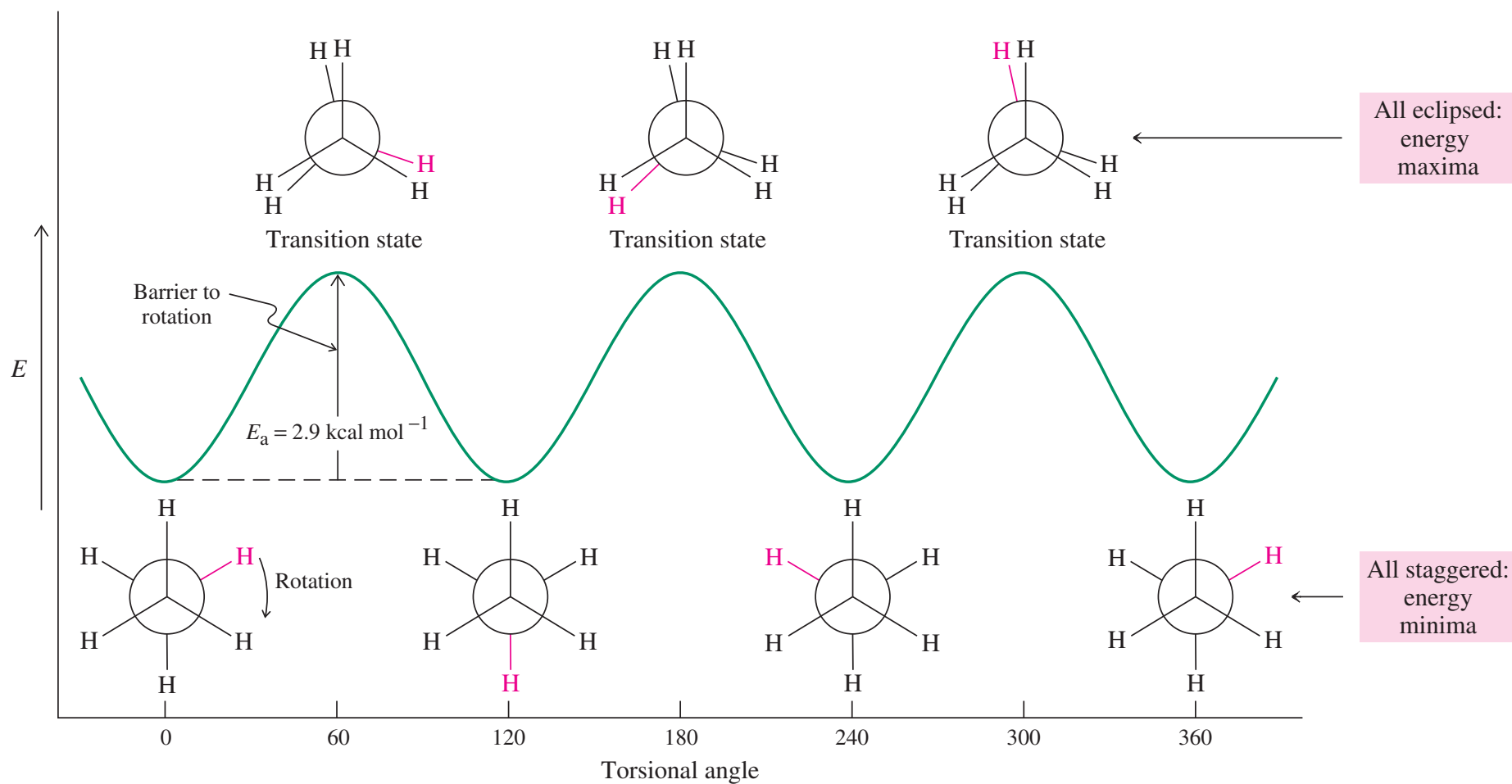
To make the three rear hydrogen atoms more visible in eclipsed conformations, they are drawn somewhat rotated out of the perfectly eclipsing position.



The staggered conformer is the most stable and lowest energy state of the molecule.

In eclipsed, the molecule has highest energy content ($2.9 \text{ kcal mol}^{-1}$) above the staggered.

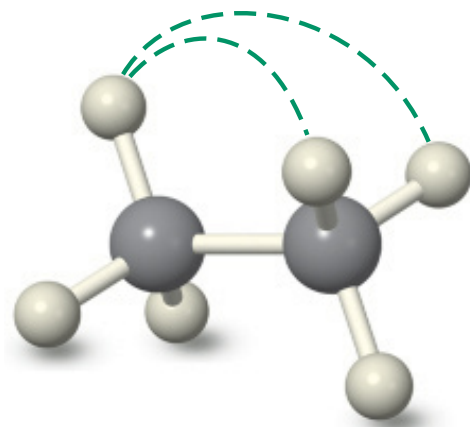
The change in energy resulting from bond rotation from the staggered to the eclipsed conformation is called **rotational** or **torsional energy**, or **torsional strain**.



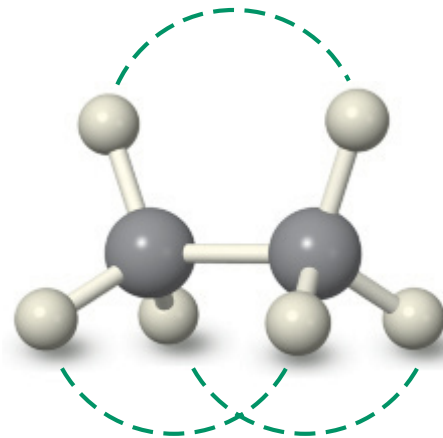
Origin of the torsional strain:

Rotation to the eclipsed geometry brings pairs of C–H bonds on the two carbons closer to each other, repulsion between the electrons in these bonds increases.

Rotation also causes subtle changes in molecular orbital interactions, weakening the C–C bond in the eclipsed conformation.



Staggered: More stable,
because facing C–H
bonds are at maximum
distance (dashed lines)

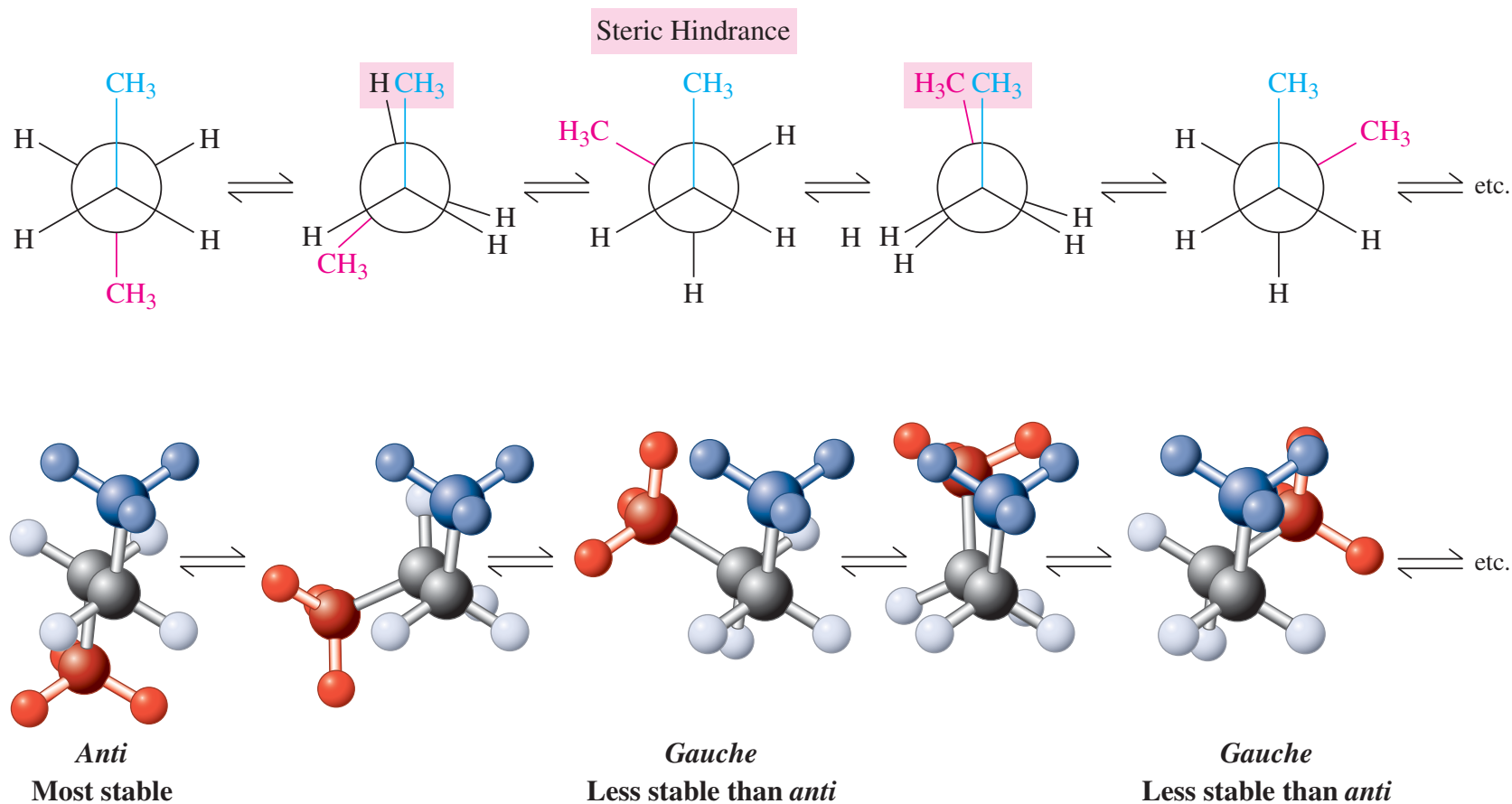


Eclipsed: Less stable,
because facing C–H
bonds are at minimum
distance (dashed lines)

Conformational analysis of butane

In staggered conformer, two methyl groups are as far away from each other, called *anti* is the most stable because **steric hindrance** is minimized.

As a consequence of steric hindrance, the *gauche* conformer is higher in energy than the *anti* conformer by about $0.9 \text{ kcal mol}^{-1}$ (3.8 kJ mol^{-1}).



Potential-energy diagram: The *anti* conformer is the most stable and most abundant in solution (about 72% at 25 °C). Its less stable *gauche* counterpart is present in lower concentration (28%).

