

# Organic Chemistry I

Mohammad Jafarzadeh

Faculty of Chemistry, Razi University

**Organic Chemistry, (9<sup>th</sup> edition)**

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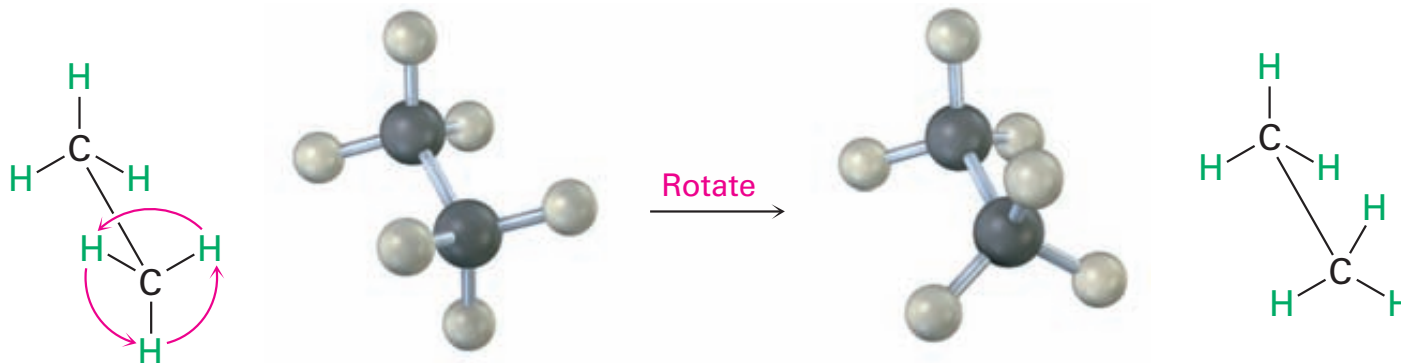
## Conformations of Ethane

**Stereochemistry** is the branch of chemistry concerned with the three-dimensional aspects of molecules. The exact three-dimensional structure of a molecule is often crucial to determining its properties and biological behavior.

The  $\sigma$  bonds are cylindrically symmetrical, and the intersection of a plane cutting through a carbon–carbon single-bond orbital looks like a circle.

Because of this cylindrical symmetry, rotation is possible around carbon–carbon bonds in open-chain molecules.

In ethane rotation around the C–C bond occurs freely, constantly changing the spatial relationships between the hydrogens on one carbon and those on the other:



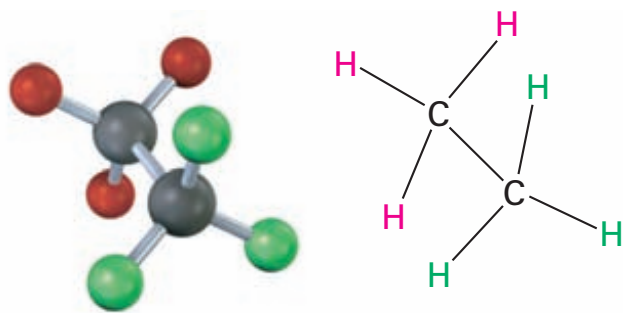
Different arrangements of atoms result from bond rotation called **conformations**, and molecules have different arrangements called conformational isomers or **conformers**.

Unlike constitutional isomers, different conformers often can't be isolated because they interconvert too rapidly.

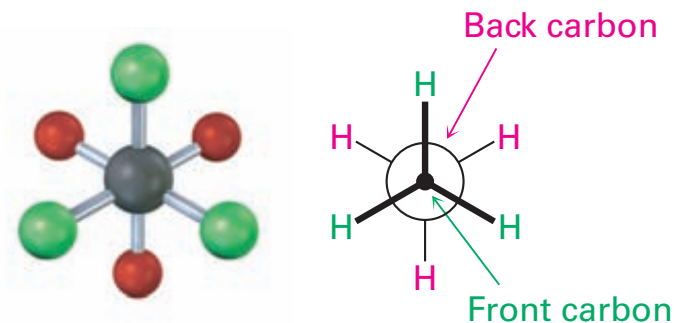
A **sawhorse representation** views the carbon–carbon bond from an oblique angle and indicates spatial orientation by showing all C–H bonds.

A **Newman projection** views the carbon–carbon bond directly end-on and represents the two carbon atoms by a circle.

Bonds attached to the front carbon are represented by lines to the center of the circle, and bonds attached to the rear carbon are represented by lines to the edge of the circle.



**Sawhorse  
representation**



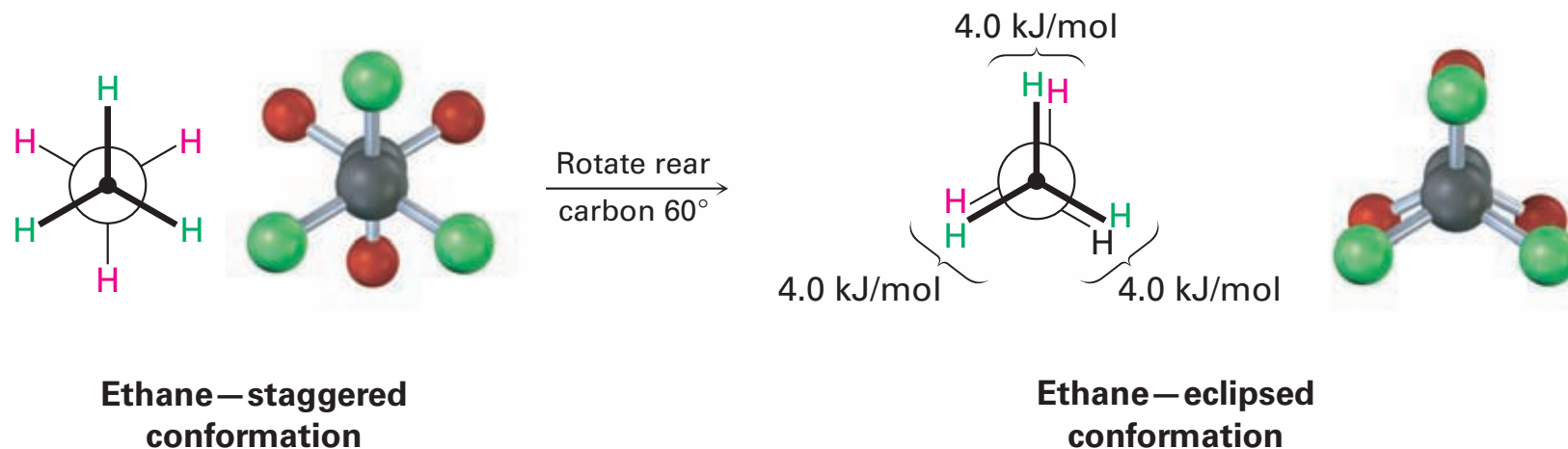
**Newman  
projection**

There is no *perfectly* free rotation in ethane. There is a small (12 kJ/mol; 2.9 kcal/mol) barrier to rotation and that some conformations are more stable than others.

The lowest-energy, most stable conformation is the one in which all six C–H bonds are as far away from one another as possible—**staggered** when viewed end-on in a Newman projection.

The highest-energy, least stable conformation is the one in which the six C–H bonds are as close as possible—**eclipsed** in a Newman projection.

At any given instant, about 99% of ethane molecules have an approximately **staggered conformation** and only about 1% are near the **eclipsed conformation**.



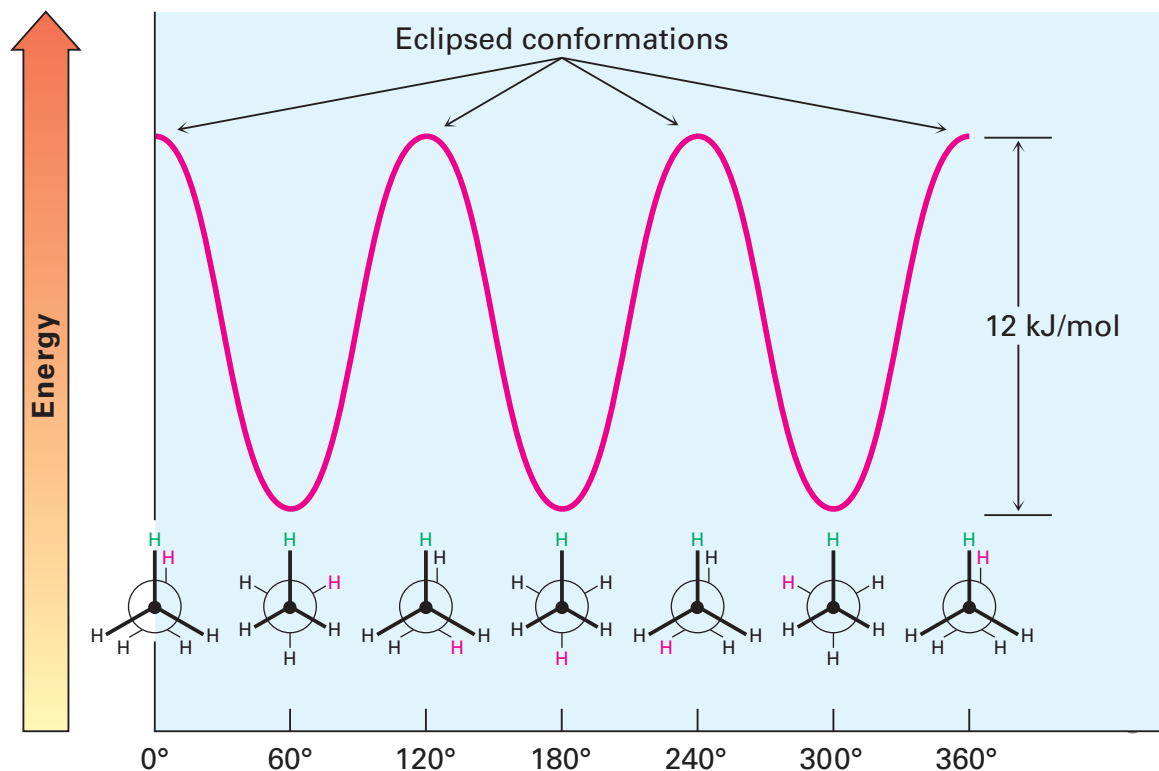
The extra 12 kJ/mol of energy present in the eclipsed conformation of ethane is called **torsional strain**.

The major factor is an interaction between C–H bonding orbitals on one carbon with antibonding orbitals on the adjacent carbon, which stabilizes the staggered conformation relative to the eclipsed one.

Total strain of 12 kJ/mol arises from three equal H–H eclipsing interactions, a value of 4.0 kJ/mol (1.0 kcal/mol) to each single interaction.

Potential energy vs. degree of rotation: the angle between C–H bonds on the front and back carbons as viewed end-on (the *dihedral angle*) goes full circle from 0 to 360°.

Energy minima occur at staggered conformations, and energy maxima occur at eclipsed conformations.

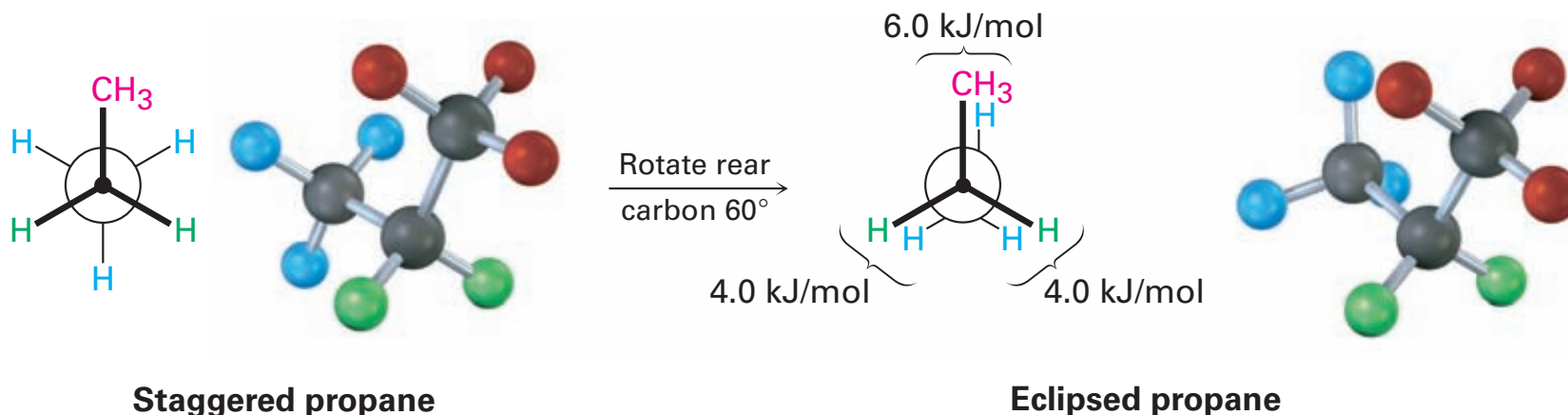


## Conformations of Other Alkanes

Propane has a torsional barrier that results in hindered rotation around the carbon–carbon bonds. The barrier is slightly higher in propane than in ethane—a total of 14 kJ/mol (3.4 kcal/mol) versus 12 kJ/mol.

The eclipsed conformation of propane has three interactions—two ethane-type hydrogen–hydrogen interactions and one additional hydrogen–methyl interaction.

Since each eclipsing  $\text{H} \longleftrightarrow \text{H}$  interaction is the same as that in ethane and thus has an energy “cost” of 4.0 kJ/mol, we can assign a value of  $14 - (2 \times 4.0) = 6.0$  kJ/mol (1.4 kcal/mol) to the eclipsing  $\text{H} \longleftrightarrow \text{CH}_3$  interaction.

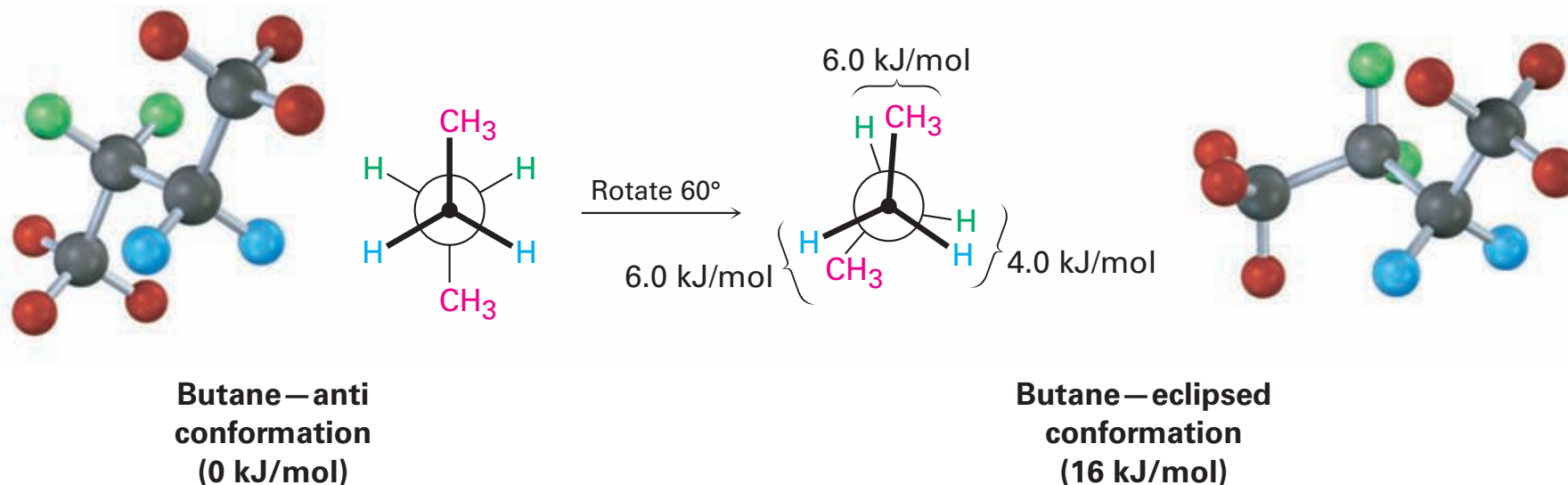


The conformational situation becomes more complex for larger alkanes because not all staggered conformations (and/or eclipsed conformations) have the same energy.

In butane, the lowest-energy arrangement, called the **anti conformation**, is the one in which the two methyl groups are as far apart as possible—180° away from each other.

As rotation around the C2–C3 bond occurs, an eclipsed conformation is reached when there are two  $\text{CH}_3 \longleftrightarrow \text{H}$  interactions and one  $\text{H} \longleftrightarrow \text{H}$  interaction.

This eclipsed conformation is more strained than the anti conformation by  $2 \times 6.0 \text{ kJ/mol} + 4.0 \text{ kJ/mol}$  (two  $\text{CH}_3 \longleftrightarrow \text{H}$  interactions plus one  $\text{H} \longleftrightarrow \text{H}$  interaction), for a total of 16 kJ/mol (3.8 kcal/mol).

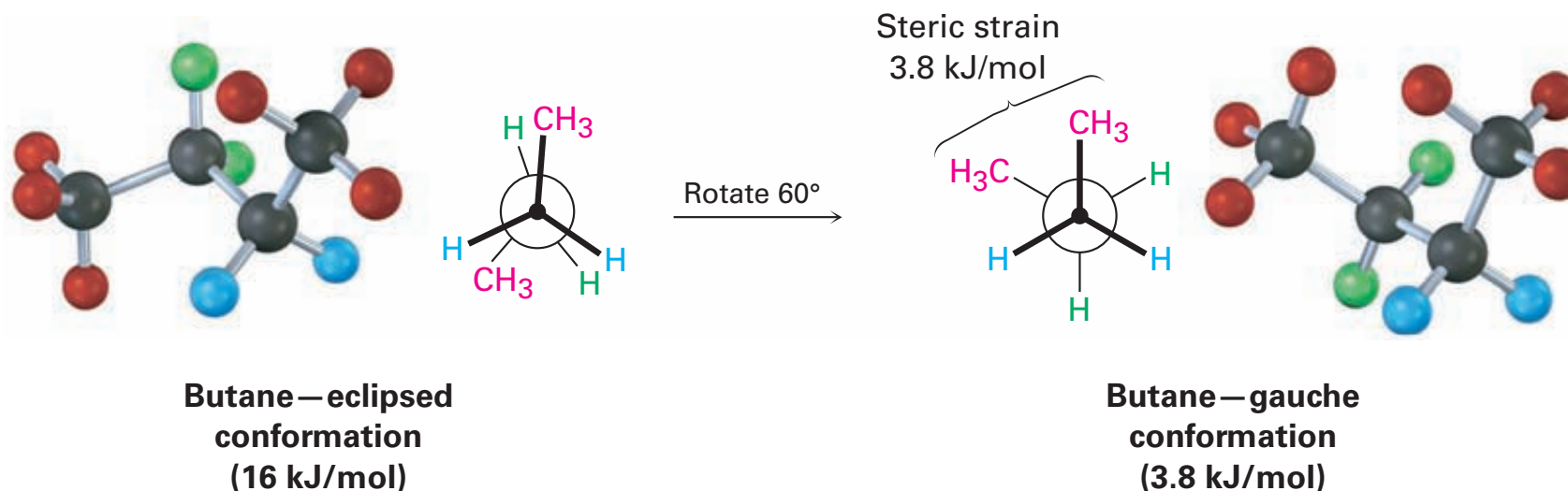


As bond rotation continues, an energy minimum is reached at the staggered conformation where the methyl groups are  $60^\circ$  apart.

Called the **gauche conformation**, it lies 3.8 kJ/mol (0.9 kcal/mol) higher in energy than the anti conformation even though it has no eclipsing interactions.

This energy difference occurs because the hydrogen atoms of the methyl groups are near one another in the gauche conformation, resulting in what is called **steric strain**.

Steric strain is the repulsive interaction that occurs when atoms are forced closer together than their atomic radii allow. It's the result of trying to force two atoms to occupy the same space.

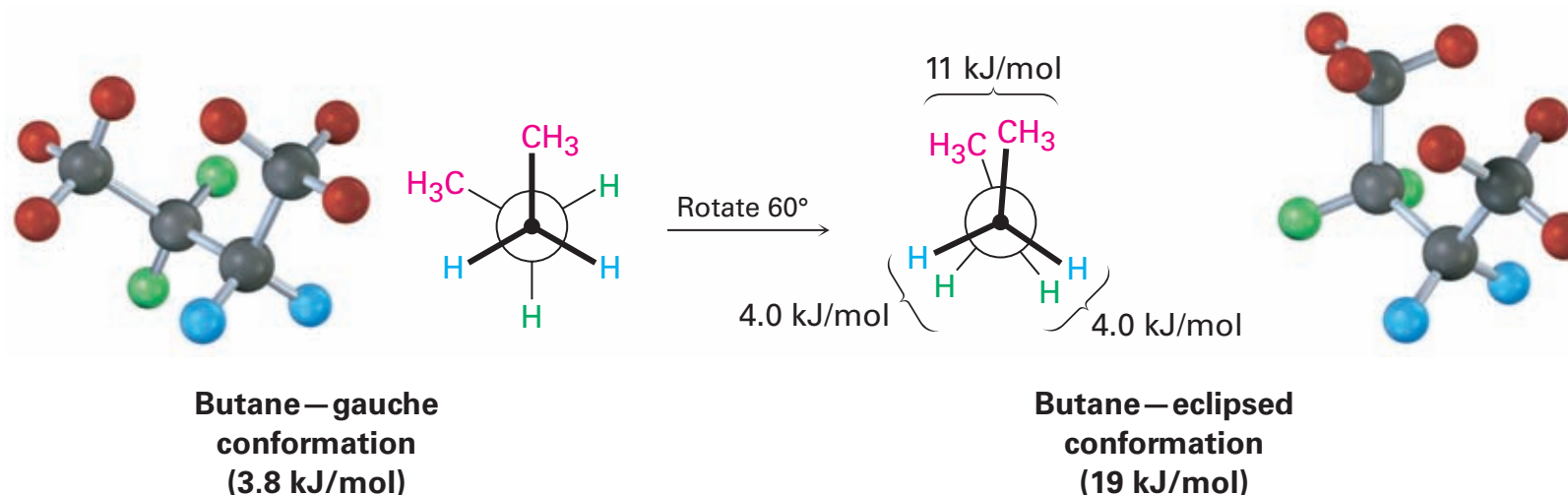




As the dihedral angle between the methyl groups approaches  $0^\circ$ , an energy maximum is reached at a second eclipsed conformation.

Because the methyl groups are forced even closer together than in the gauche conformation, both torsional strain and steric strain are present.

A total strain energy of 19 kJ/mol (4.5 kcal/mol) has been estimated for this conformation, making it possible to calculate a value of 11 kJ/mol (2.6 kcal/mol) for the  $\text{CH}_3 \longleftrightarrow \text{CH}_3$  eclipsing interaction: total strain of 19 kJ/mol minus the strain of two  $\text{H} \longleftrightarrow \text{H}$  eclipsing interactions ( $2 \times 4.0 \text{ kcal/mol}$ ) equals 11 kJ/mol.



## Potential energy versus rotation about the C2–C3 bond:

