ORGANIC CHEMISTRY-SEM-2H

CONFORMATIONAL ANALYSIS

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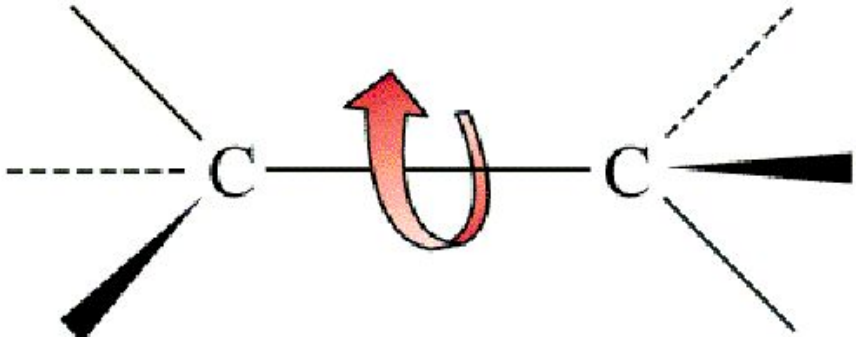
Syllabus: Conformation: conformational nomenclature: eclipsed, staggered, gauche, syn and anti; dihedral angle, torsion angle; Klyne-Prelog terminology; P/M descriptors; energy barrier of rotation, concept of torsional and steric strains;

Relative stability of conformers on the basis of steric effect, dipole-dipole interaction and H-bonding; butane gauche interaction; conformational analysis of ethane, propane, n-butane, 2methylbutane and 2,3-dimethylbutane; haloalkane, 1,2-dihaloalkanes and 1,2-diols (up to four carbons); 1,2-halohydrin; conformation of conjugated systems (s-cis and s-trans).

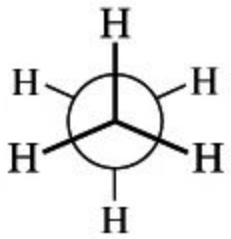
Conformations of Alkanes: Rotation about C-C Single Bonds

- Different spatial arrangements of atoms that result from rotation about carbon-carbon single bonds are known as **conformations**
- Different conformations also are called **conformational isomers** or **conformers**



Newman Projections

- A convenient way to describe conformation isomers is to look at the molecule along the axis of the bond of interest
- A **Newman projection** is a graphical representation of such a view



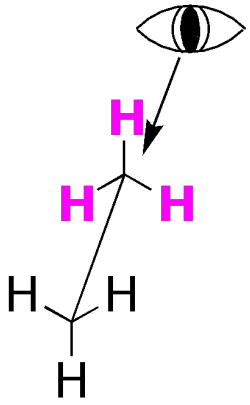
Ch. 3: Alkanes and Cycloalkanes: Conformations and cis-trans Stereoisomers

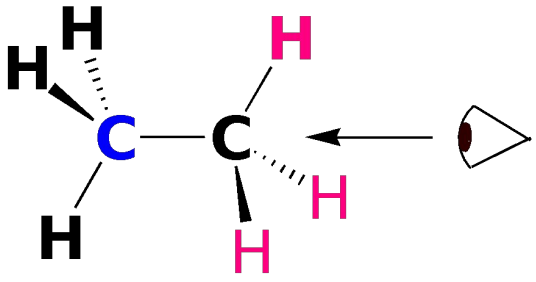
Stereochemistry: three-dimensional aspects of molecules

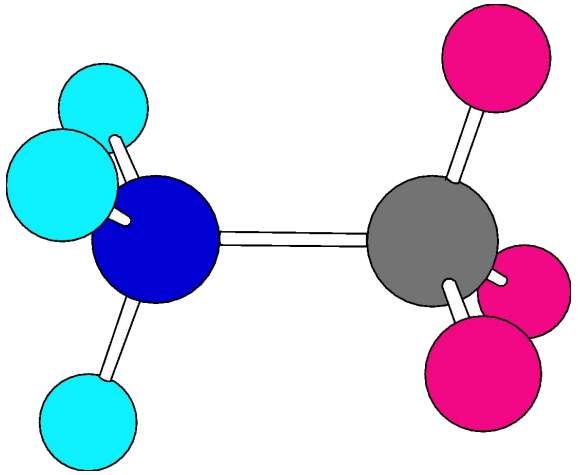
Conformation: different spatial arrangements of atoms that result from rotations about single (σ) bonds

Conformer: a specific conformation of a molecule

3.1: Conformational Analysis of Ethane

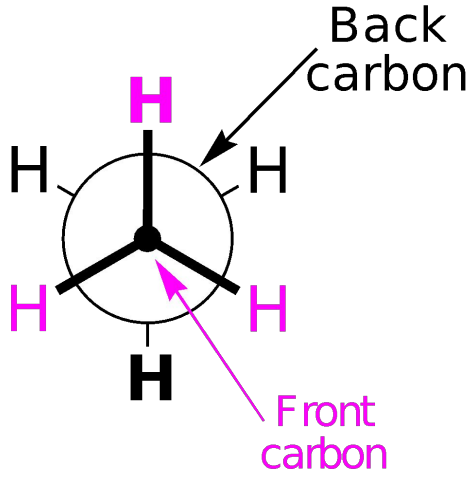




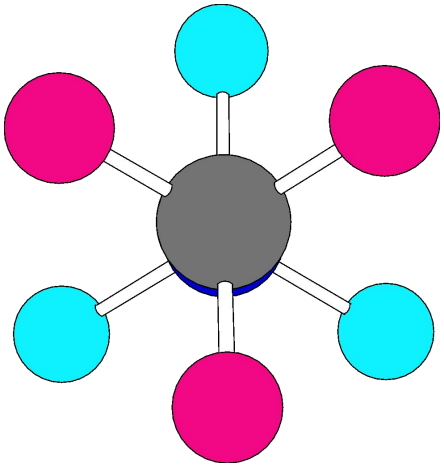


Sawhorse

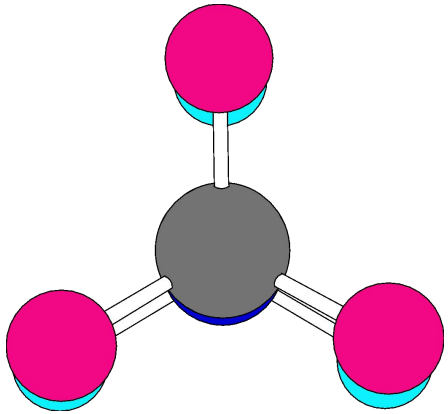
There are two conformations of ethane:



Newman projection



Staggered



Eclipsed

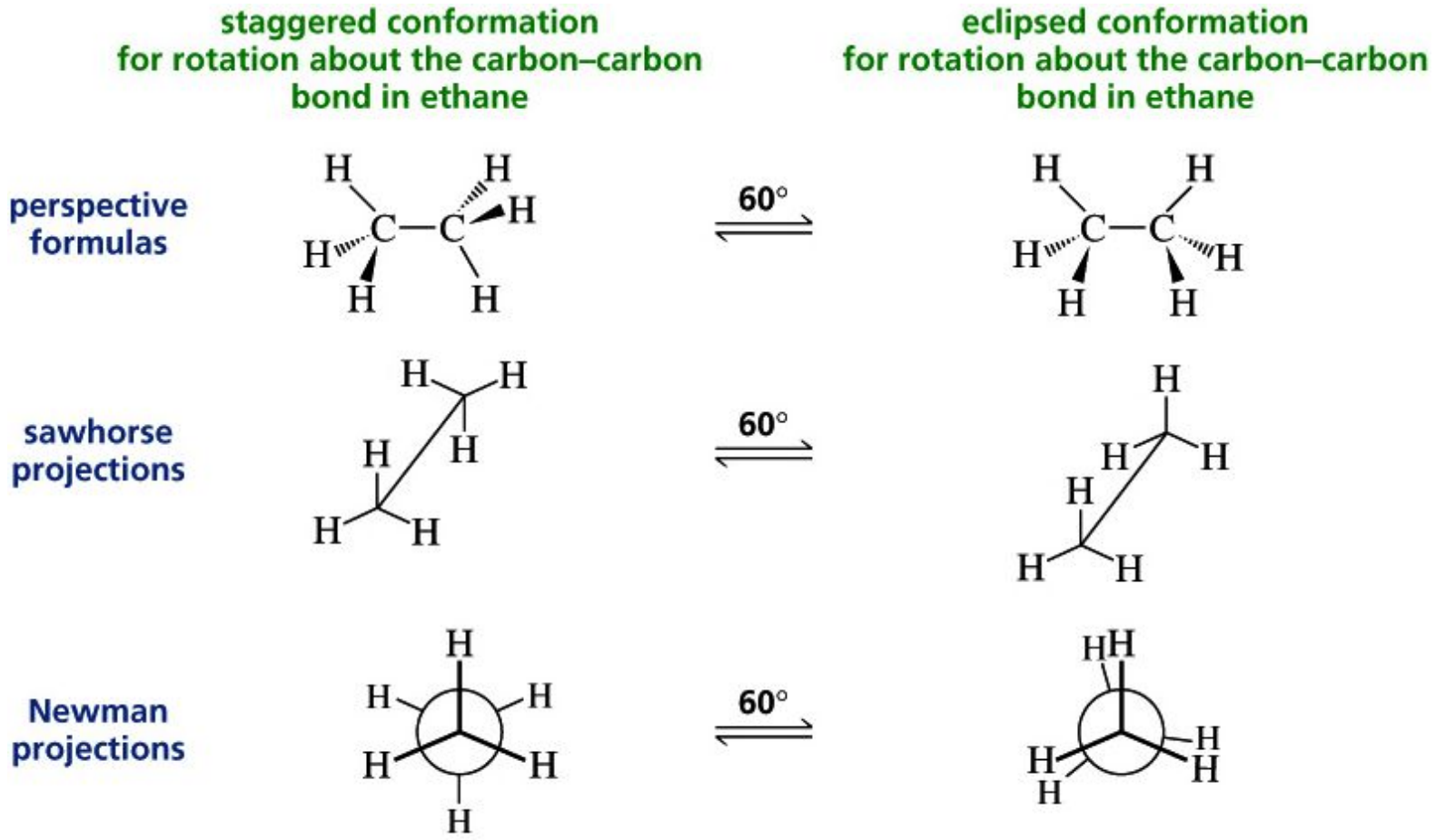
Dihedral (torsion) angle: angle between an atom (group) on the front atom of a Newman Projection and an atom (group) on the back atom

Dihedral angles of ethanes:

Staggered conformation: 60° (gauche), 180° (anti), and 300° (-60°, gauche)

Eclipsed conformation: 0°, 120°, and 240° (-120°)

Conformations of Alkanes: Rotation About C-C Single Bonds

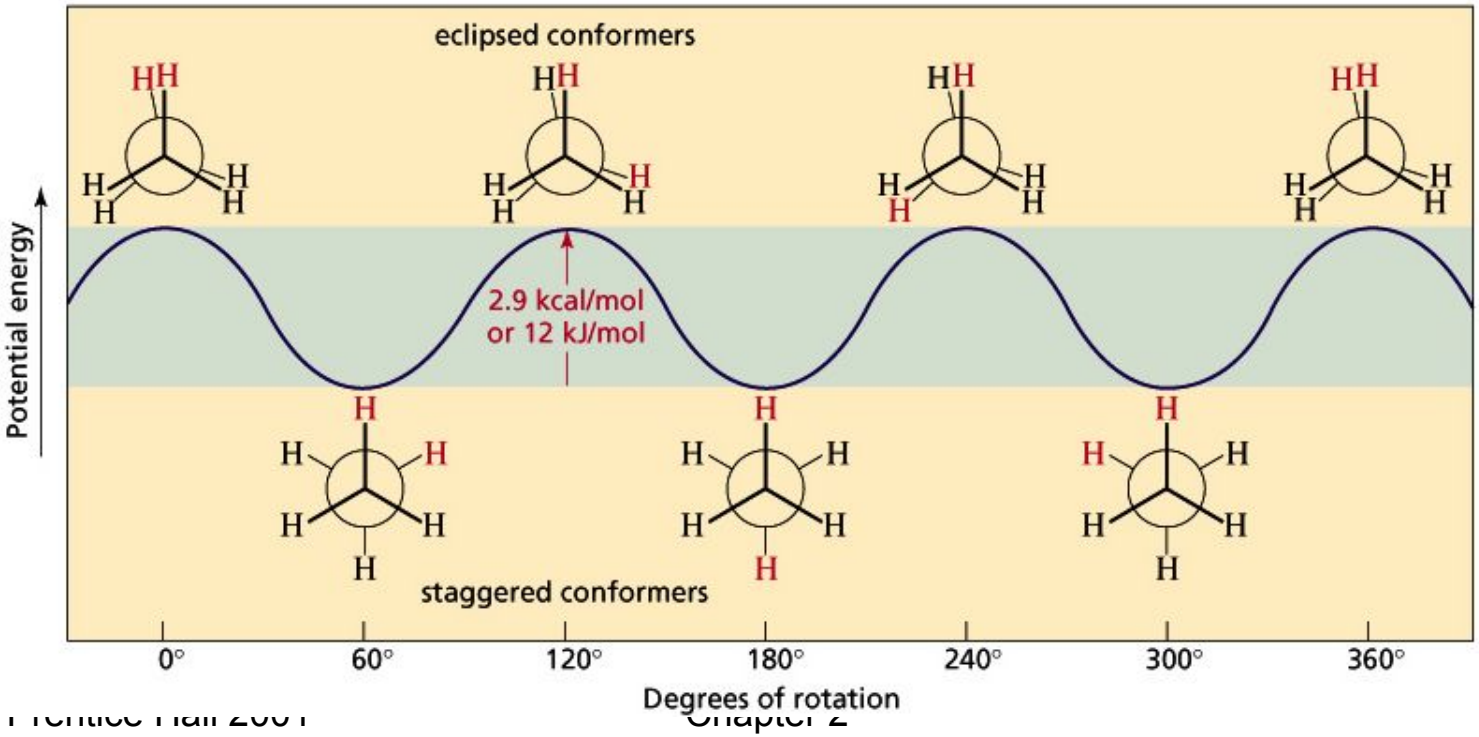


Conformations of Alkanes: Rotation About C-C Single Bonds

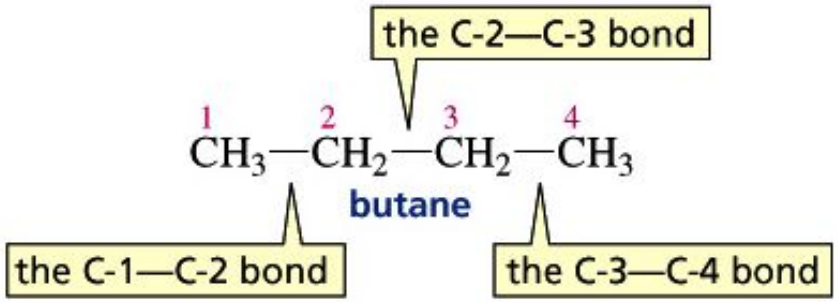
- Rotation about the C-C bond of ethane is not completely free
- Electrons of C-H bonds repel electrons of other C-H bonds if they get too close together
- For these reasons the eclipsed conformation is not as stable as the staggered conformation

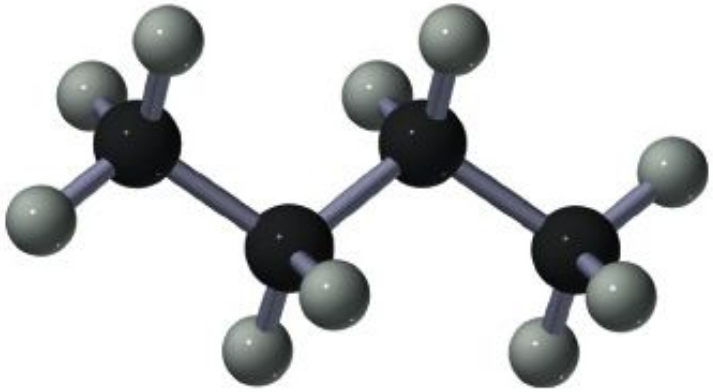
Conformations of Alkanes: Rotation About C-C Single Bonds

- The extra energy of the eclipsed conformation is called **Torsional Strain**

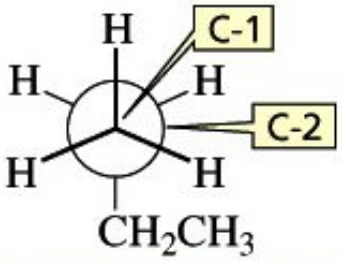


Conformations of Butane: Rotation About the C_2-C_3 Single Bond

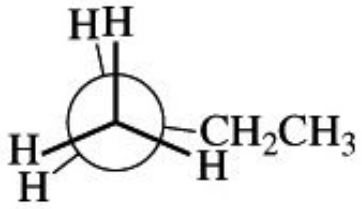




ball-and-stick model of butane

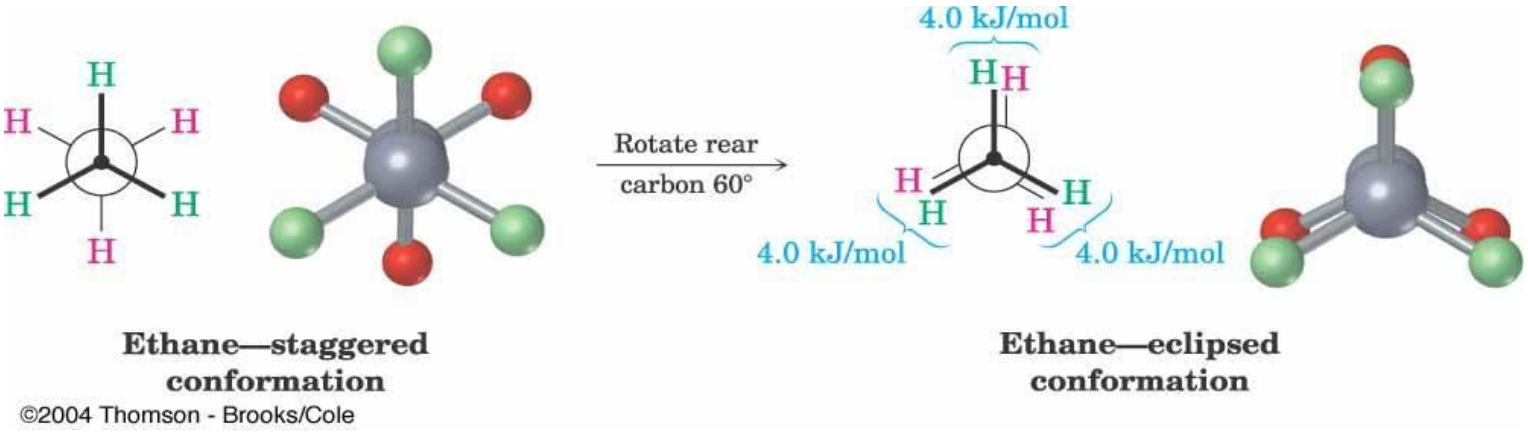


staggered conformation for rotation about the C-1—C-2 bond in butane



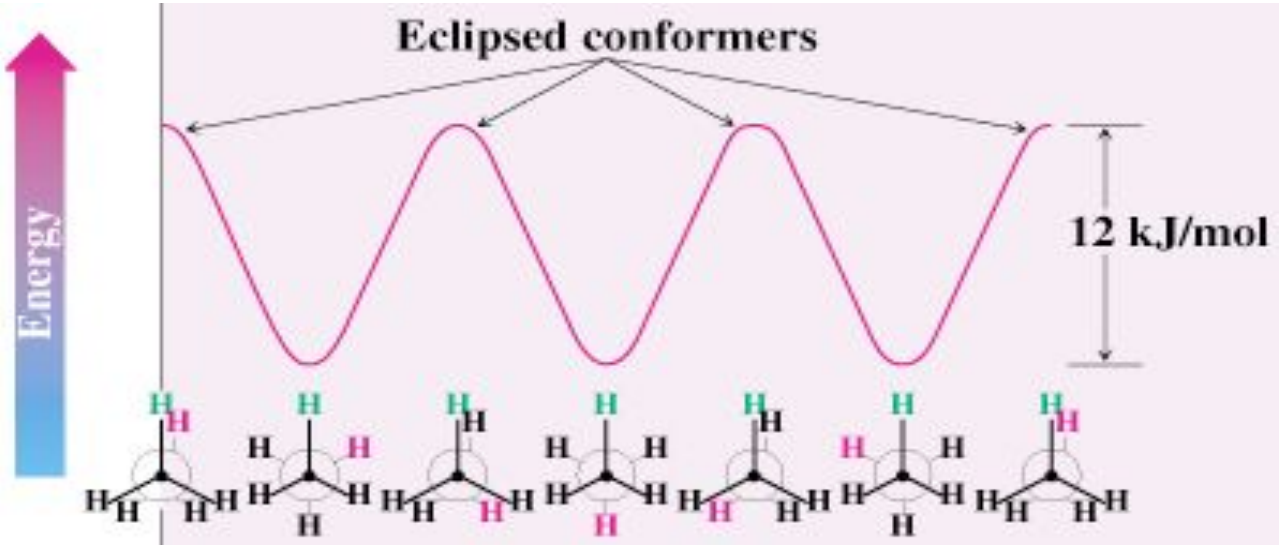
eclipsed conformation for rotation about the C-1—C-2 bond in butane

Ethane's Conformations

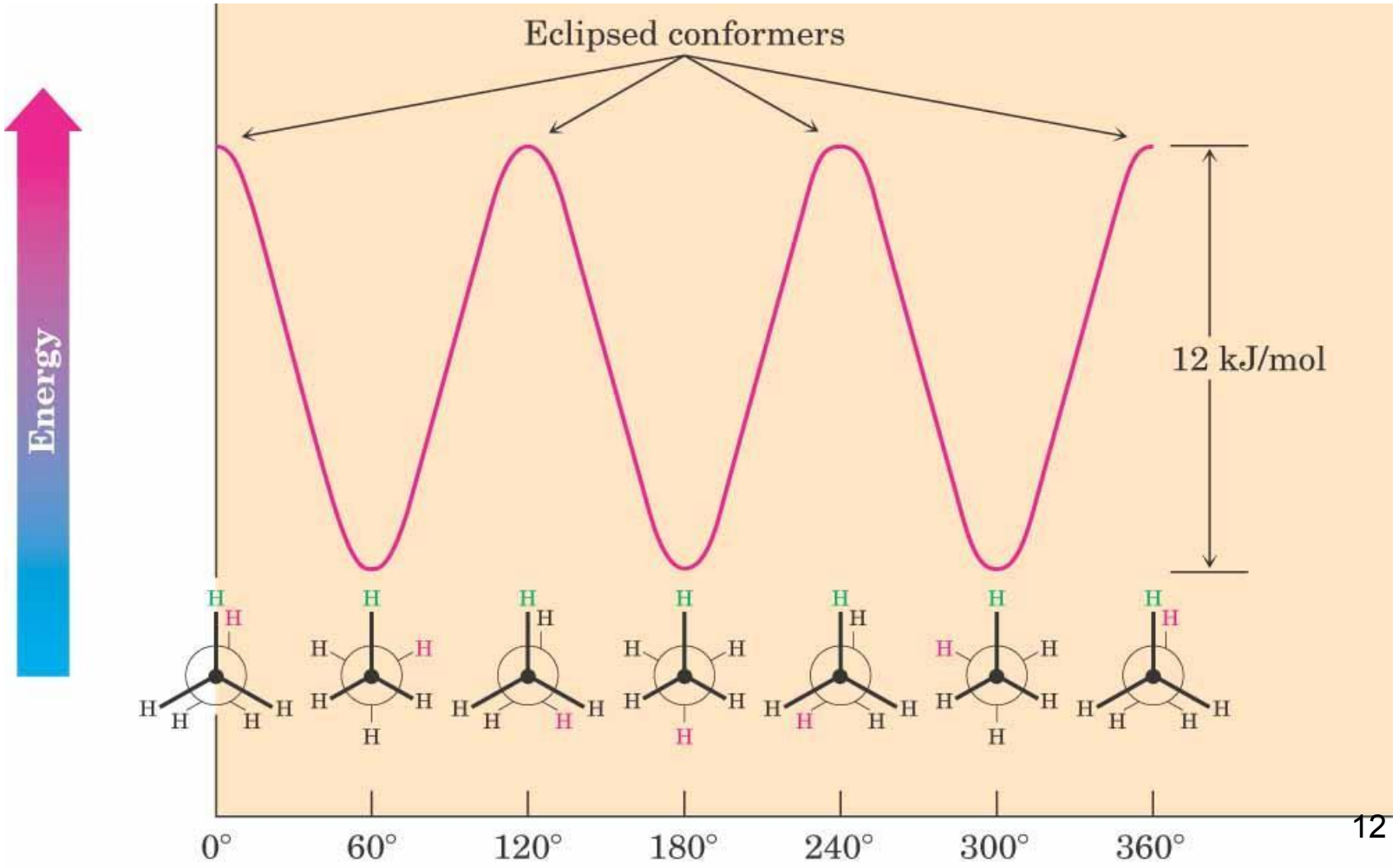


Ethane's Conformations

- There barrier to rotation between conformations is small (12 kJ/mol; 2.9 kcal/mol) The most stable conformation of ethane has all six C–H bonds away from each other (**staggered**)
- The least stable conformation has all six C–H bonds as close as possible (**eclipsed**) in a Newman projection – energy due to torsional strain

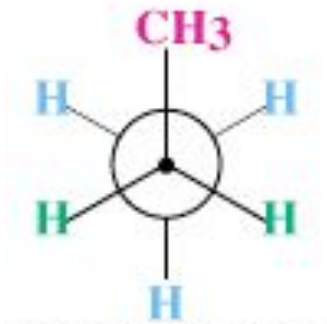


Ethane's Conformations



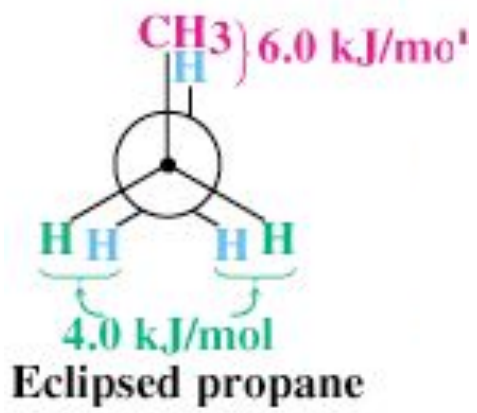
2.2 Conformations of Propane

- Propane (C_3H_8) torsional barrier around the carbon–carbon bonds 14 kJ/mol



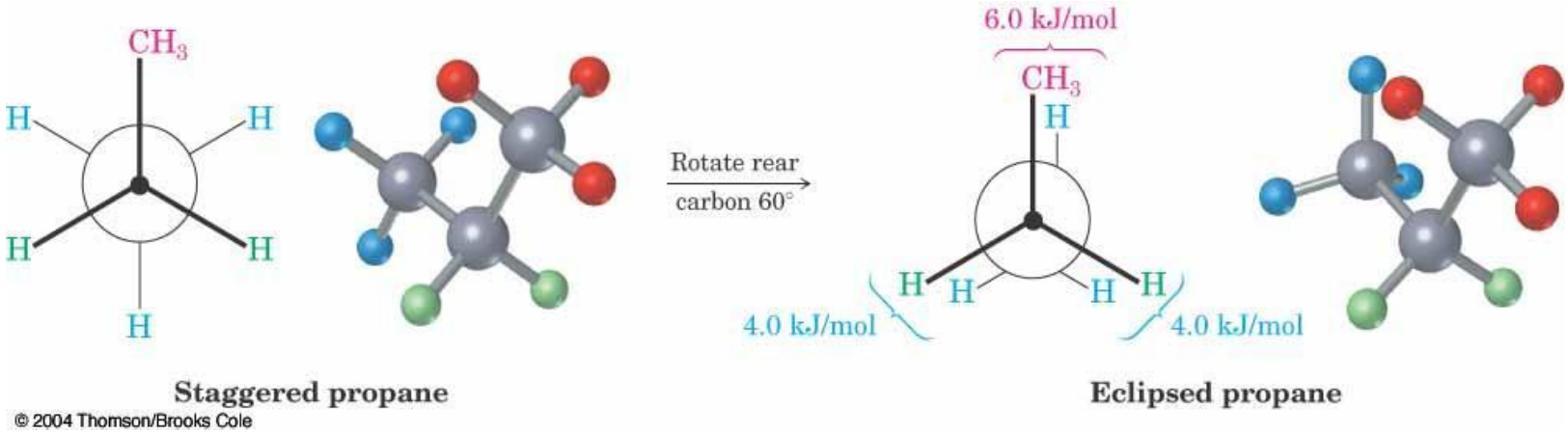
Staggered propane

- Eclipsed conformer of propane has two ethane-type H–H interactions and an interaction between C–H and C–C bond



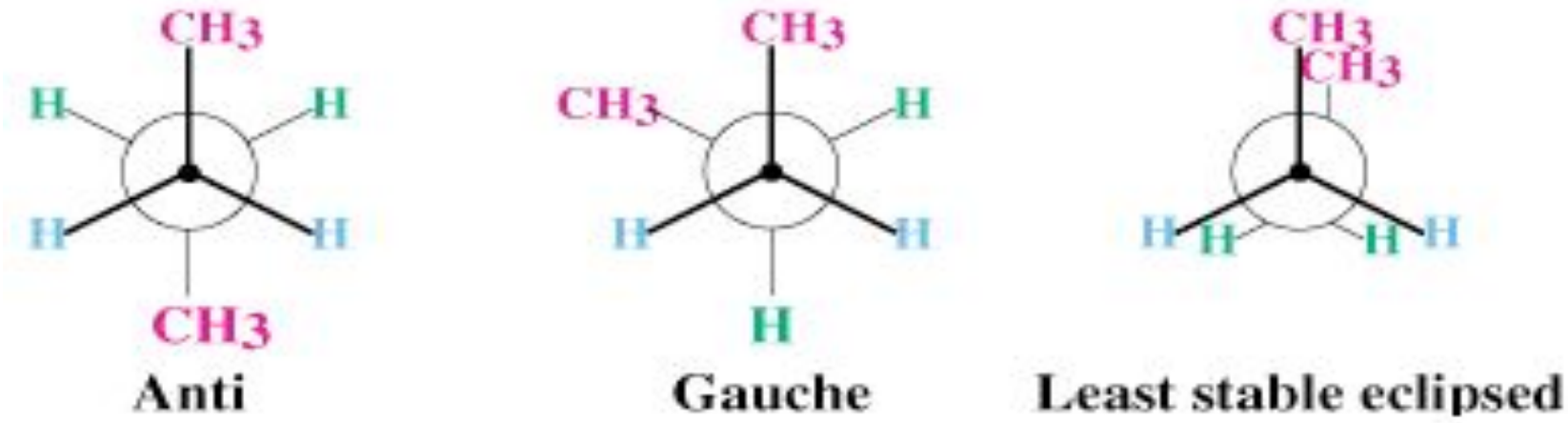
Eclipsed propane

Propane conformations

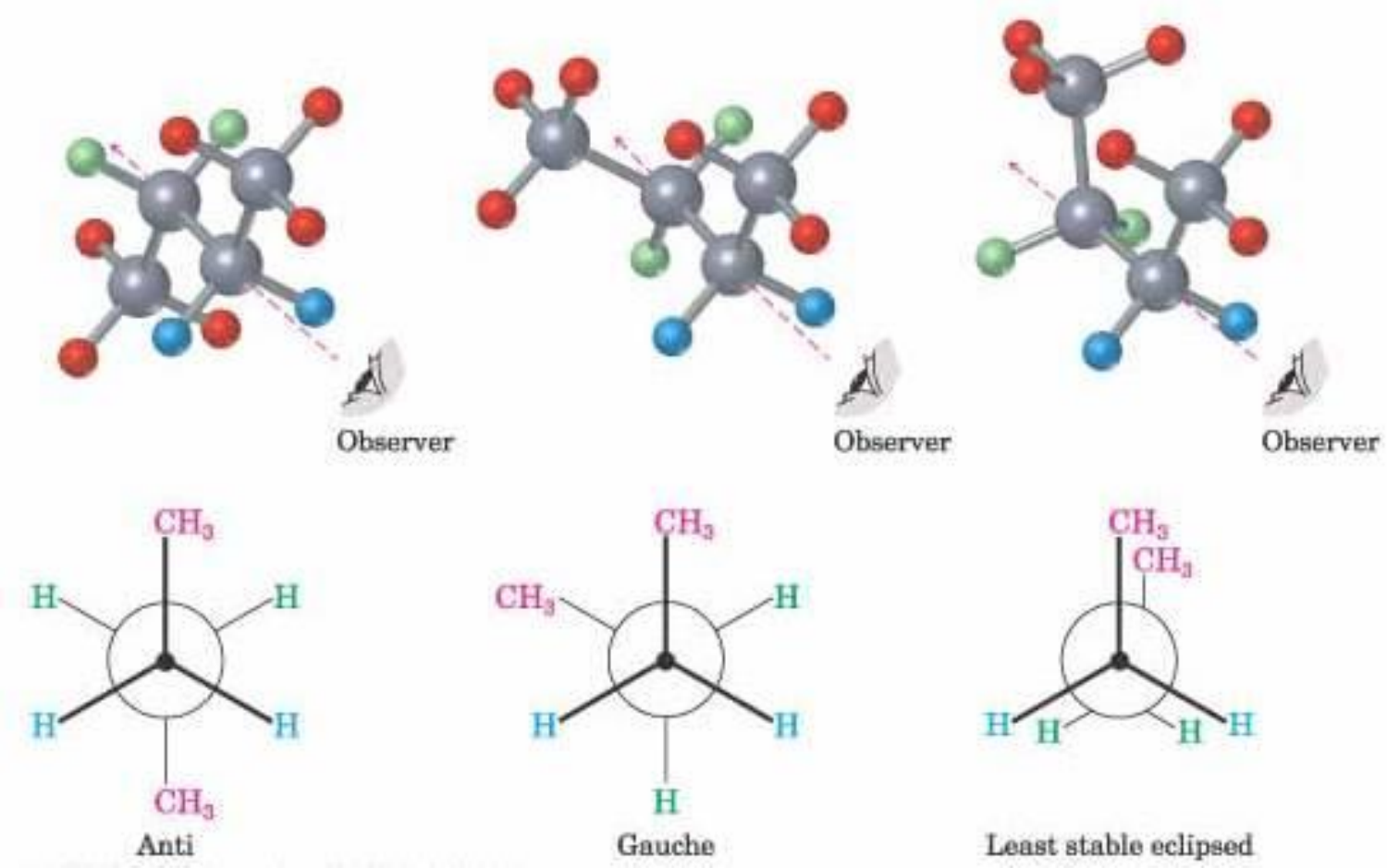


2.3 Conformations of Butane

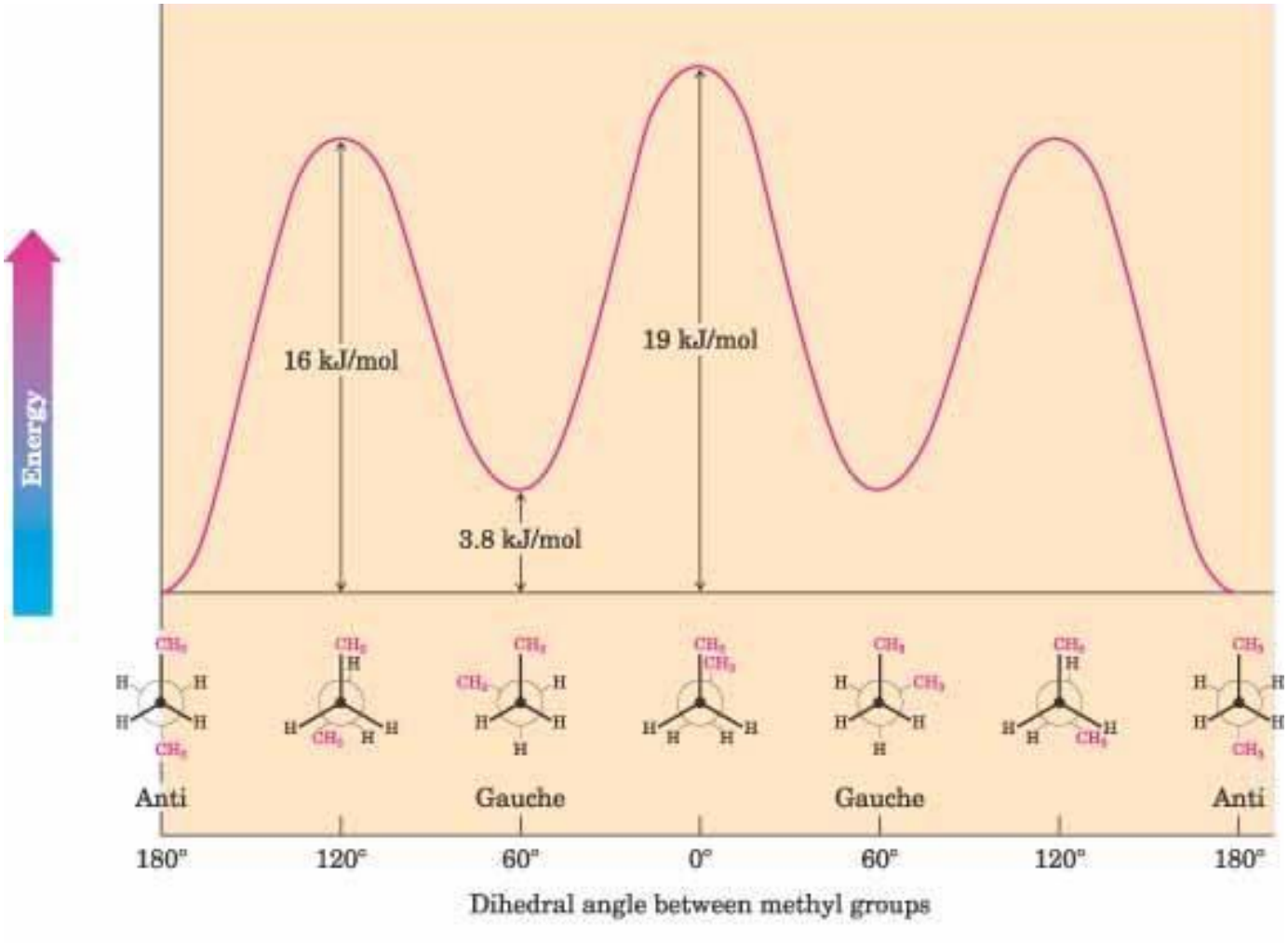
- **anti conformation** has two methyl groups 180° away from each other
- Rotation around the C2–C3 gives eclipsed conformation
- Staggered conformation with methyl groups 60° apart is **gauche conformation**



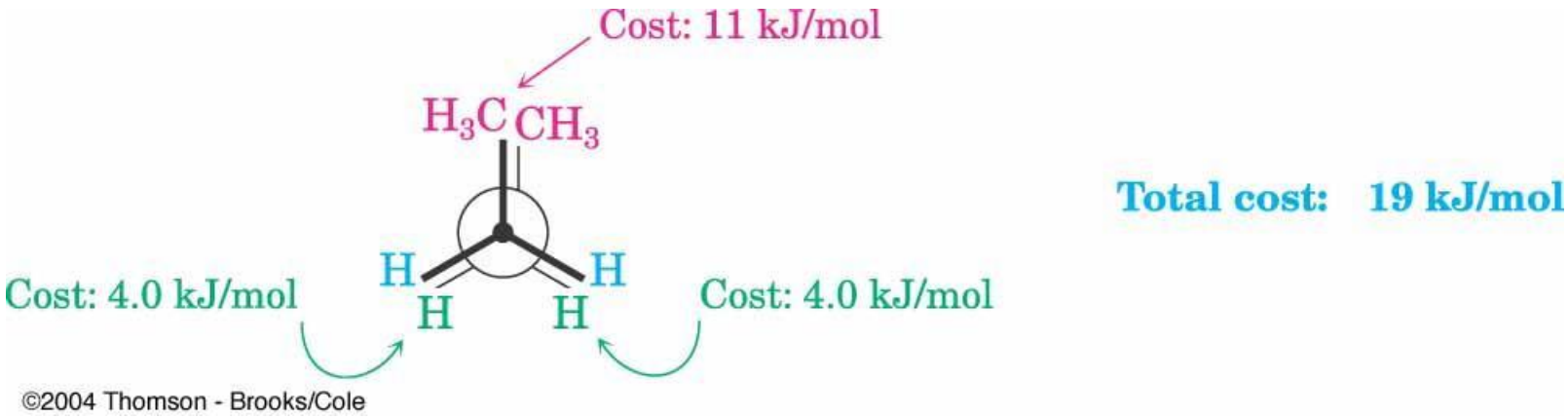
Conformations of Butane



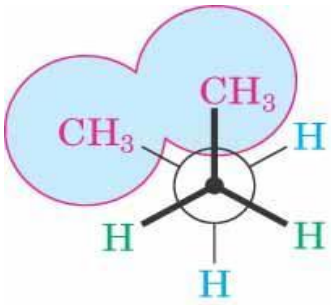
Conformations of Butane

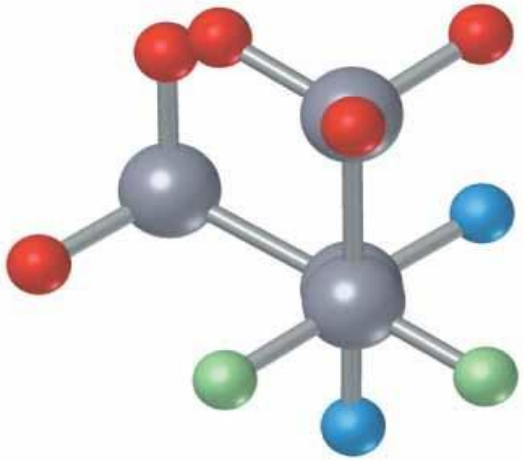


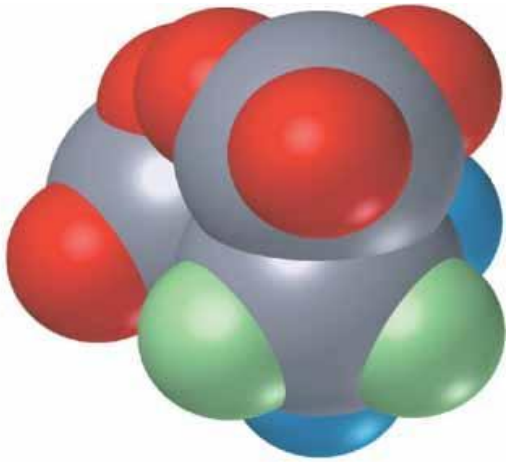
Eclipsed Conformations of Butane



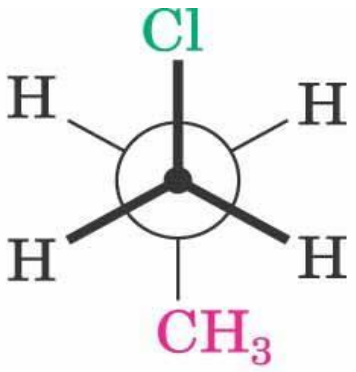
Gauche conformation: steric strain



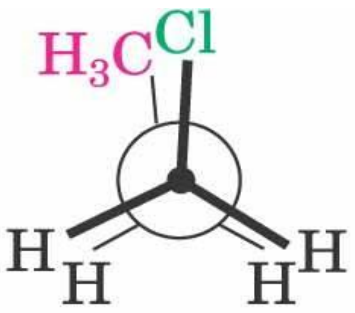




1-chloropropane

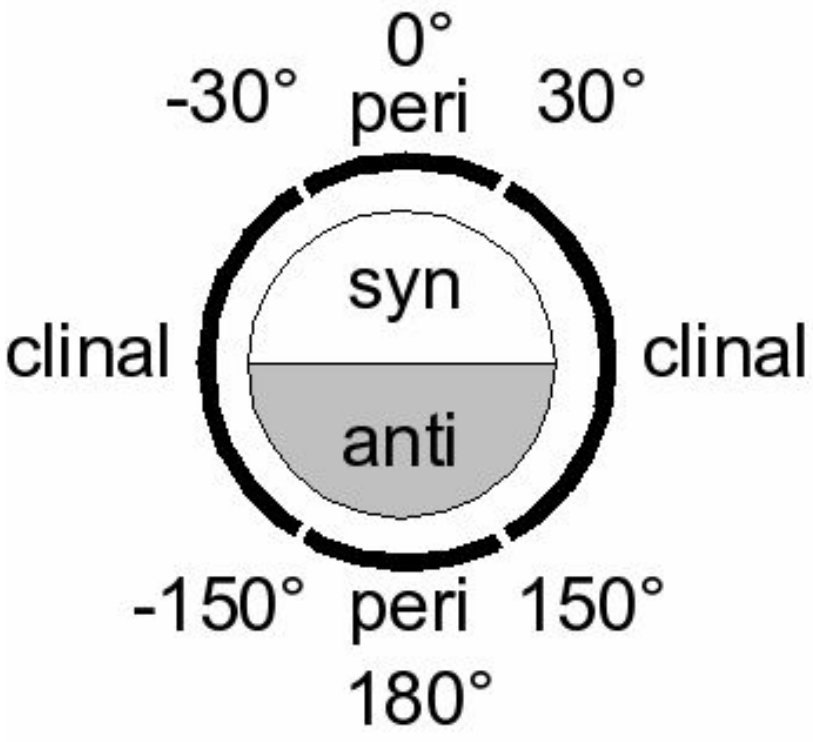


Most stable (staggered)



Least stable (eclipsed)

Klyne-Prelog terminology of Conformations



syn/anti peri/clinal

Many definitions that describe a specific conformer (IUPAC Gold Book) exist, developed by William Klyne and Vladimir Prelog, constituting their Klyne–Prelog system of nomenclature:

- a torsion angle of ±60° is called **gauche [g]**
- a torsion angle between 0° and ± 90° is called **syn (s)**
- a torsion angle between ± 90° and 180° is called **anti (a)**
- a torsion angle between 30° and 150° or between –30° and –150° is called **clinal (c)**
- a torsion angle between 0° and ±30° or ±150° and 180° is called **periplanar (p)**

 a torsion angle between 0° to 30° is called **synperiplanar or syn- or cis-conformation (sp)**

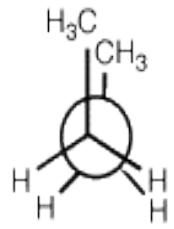
 a torsion angle between 30° to 90° and –30° to –90° is called **synclinal or gauche or skew (sc)[g]**

 a torsion angle between 90° to 150°, and –90° to –150° is called **anticlinal (ac)**

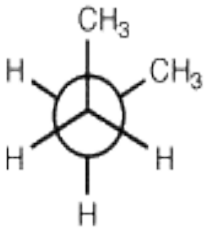
 a torsion angle between ± 150° to 180° is called **antiperiplanar or anti or trans (ap).**

Torsional strain results from resistance to twisting about a bond.

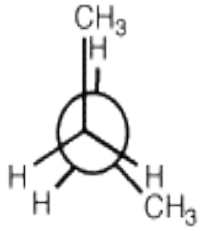
Conformations of butane: N & Relative stabilities



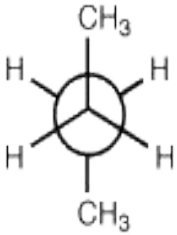
Dihedral angle 0°
SYNPERIPLANAR
least stable eclipsed



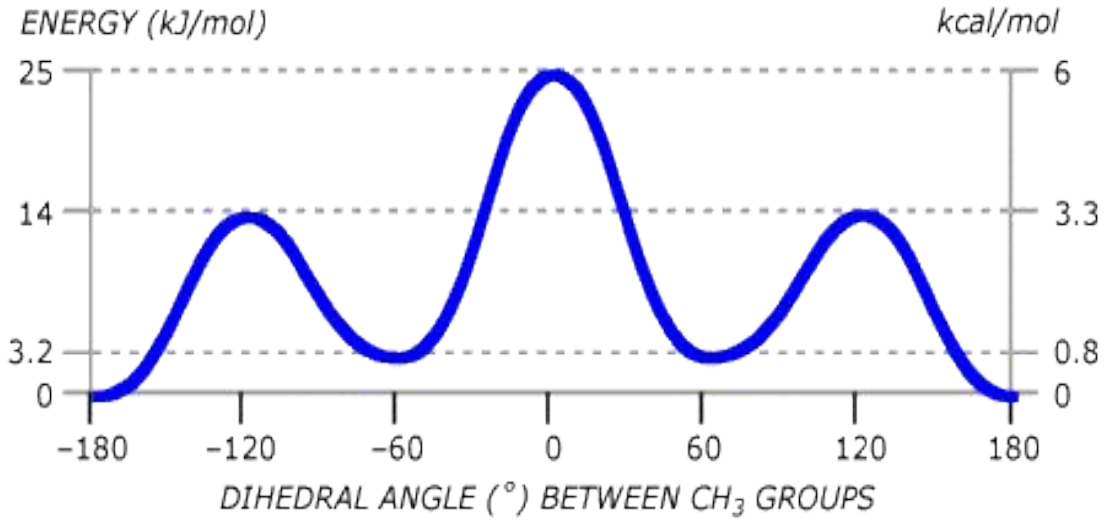
60°
GAUCHE



120°
ANTICLINAL
eclipsed



180°
ANTIPERIPLANAR
most stable



synperiplanar has **two** different types of strain:

TORSIONAL STRAIN
Three eclipsed pairs of bonds (total cost about 12 kJ/mol)

STERIC STRAIN
Eclipsed [CH_3–CH_3] (costs about 13 kJ/mol)

gauche is less stable than ***anti***:

STERIC STRAIN
Gauche [CH_3–CH_3] costs 3.2 kJ/mol

Torsional Strain & Steric Strain

Torsional Strain: When rotating a molecule around a bond, the **torsional strain** is the repulsion caused by the electrons in between different groups when they pass by each other. 3. **Steric Strain**: **Strain** caused by the electrons in between different groups.

Torsional strain or eclipsing **strain** is the increase in potential energy of a molecule due to repulsion between electrons in bonds that do not share an atom. eg: Consider two conformations of ethane: The smallest dihedral angle is 60º in 1; it is 0º in 2. ... Consequently, **torsional strain** is greater in 2 than in 1.

QUESTIONS

1. **The gauche conformation of ethylene glycol is more stable than the anti conformation. Offer an explanation with structures.**
2. **The intramolecular H-bonding in *active*-butan-2,3-diol is relatively stronger than that in *messo*-butan-2,3-diol; Explain.**
3. **Draw the most stable & least stable conformers of n-butane for the rotation about C2-C3 sigma bond and label with Klyne-Prelog terminology of Conformations.**
4. **Explain why the gauche conformation of 1-chloropropane is found to be more stable than its anti form.**
5. **What do you mean by torsional angle and dihedral angle?**