CHEMISTRY

43rd class, Date : 10-11-2021

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Last class….

- Isomersim in organic compounds
- 3-D representation

In this class….

- Conformational analysis, continuation
- Stereochemistry

Organic chemistry

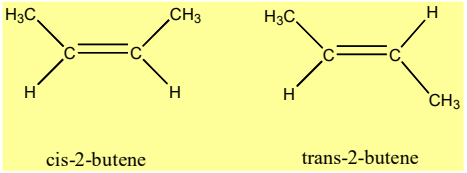
- Isomerism : Structural and stereo isomerism
- Conformational analysis
- Absolute configuration : CIP rules (naming enantiomers)
- Reactions : Substitution, Elimination, Oxidation, Reduction, Addition, Cyclisation and C-C bond formation reactions
- Synthesis of pharmaceutical products, few examples

Review of Isomerism

- ***Isomers*** – Compounds that have the same molecular formula but do not have identical structures. Generally classified into two types:
- ***Constitutional Isomers*** – differ in the way their atoms are connected
- ***Stereoisomers*** – differ in the way their atoms are arranged in space

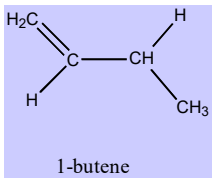
Review of Isomerism

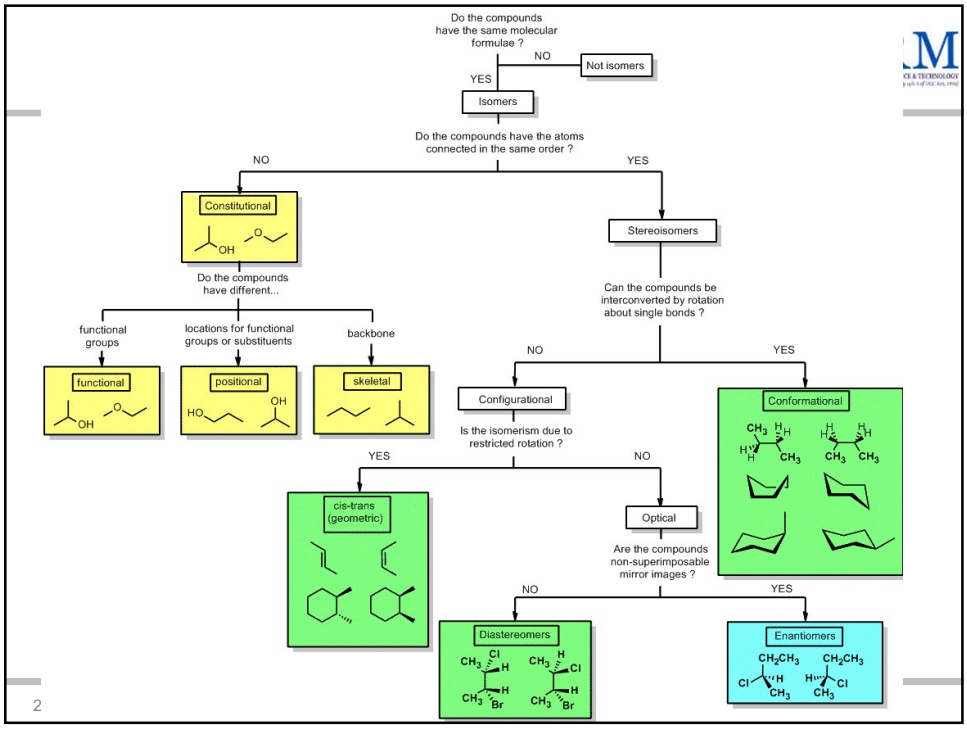
E.g., C_4H_8



Stereo

Constitutional





Review of Isomerism

Structural isomerism, or **constitutional isomerism** is a form of isomerism in which molecules with the **same molecular formula have different bonding patterns and atomic organization**, as opposed to stereoisomerism, in which molecular bonds are always in the same order and only spatial arrangement differs.

Two isomers of butane, C_4H_{10}

$$CH_3-CH_2-CH_2-CH_3$$

n-butane

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

Iso-butane

Types of Structural Isomerism

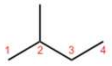
1) Chain Isomers
2) Position Isomers
3) Functional Isomers
4) Metamerism
5) Tautomerism

Structural Isomers

CHAIN ISOMERISM

In **chain isomerism**, or **skeletal isomerism**, components of the (usually carbon) **skeleton are distinctly re-ordered** to create different structures.

n-pentane
(often called simply "pentane")



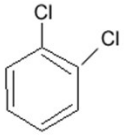
isopentane
(2-methylbutane)

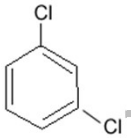
neopentane
(dimethylpropane)

POSITION ISOMERISM

Isomerism caused by the difference in the position of functional group in the same chain is termed as **position isomerism (regioisomerism)**

o-dichlorobenzene





m-dichlorobenzene

Hexane, C_6H_{14}

Formulae	*IUPAC names*
1. $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$	Hexane
2. $CH_3 - CH_2 - CH_2 - CH(CH_3) - CH_3$	2-methyl pentane
3. $CH_3 - CH_2 - CH(CH_3) - CH_2 - CH_3$	3-Methylpentane
4. $CH_3 - CH(CH_3) - CH(CH_3) - CH_3$	2, 3-Dimethyl-butane
5. $CH_3 - C(CH_3)_2 - CH_2 - CH_3$	2, 2-Dimethylbutane

Structural Isomers

FUNCTIONAL ISOMERISM

Functional isomers have same molecular formula but different functional group

Ethyl Alcohol Dimethyl Ether

METAMERISM

This type of isomerism is due to the **unequal distribution of carbon atoms on either side of functional group**. Metamerism belongs to same homologous series.

Diethyl Ether Methyl Propyl Ether

Structural Isomers

TAUTOMERISM

Tautomers are constitutional isomers that differ from each other in the **locations of a hydrogen atom and one or more double bonds** and interconvert rapidly. The **carbon skeleton of the compound is unchanged**. A reaction which **involves simple proton transfer in an intramolecular fashion is called a tautomerism**

Keto-enol tautomerism is a very common process, and is acid or base catalysed. Typically the 'keto' form of the compound is more stable, but in some instances the 'enol' form can be the more stable

An equilibrium exists between the two forms

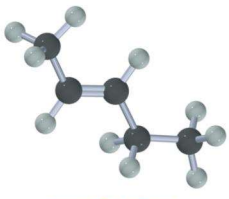
Stereoisomers

- Stereochemical isomers are molecules, which have the **same chemical formula and bond connectivity but different relative arrangement in three-dimensional space**
- Stereochemistry is the study of the **relative arrangement of atoms or groups in a molecule in three dimensional space**
- In contrast, constitutional isomers have same molecular formula but different bond connectivity

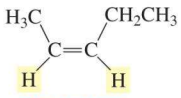
Cis-trans isomers

- Differ in the arrangement of their atoms in space

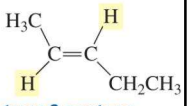
cis-2-pentene



trans-2-pentene



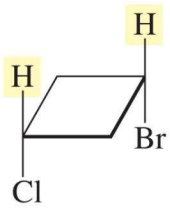
cis-2-pentene



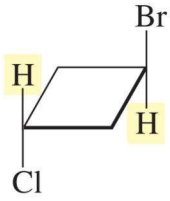
trans-2-pentene

Cis-trans isomers

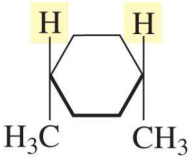
Cyclic structure



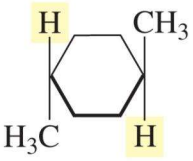
***cis*-1-bromo-3-chlorocyclobutane**



***trans*-1-bromo-3-chlorocyclobutane**

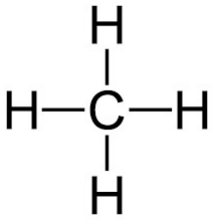


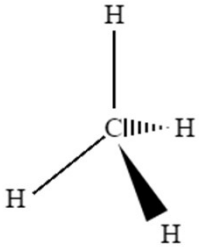
***cis*-1,4-dimethylcyclohexane**

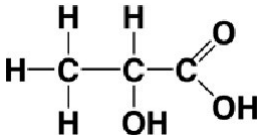


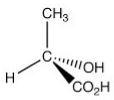
***trans*-1,4-dimethylcyclohexane**

3-D representation

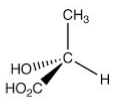






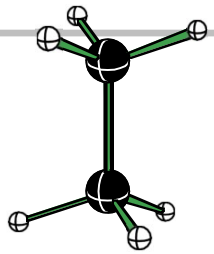


(*R*)–lactic acid

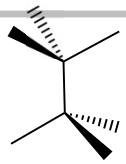


(*S*)–lactic acid

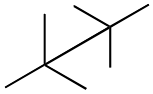
Representation of 3-D-ETHANE



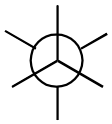
3D Image



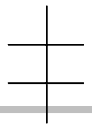
Wedge – Dash or
Flying - Wedge formula



Sawhorse projection



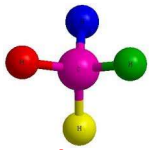
Newman Projection



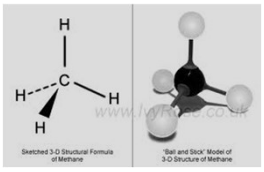
Fischer Projection

Wedge – Dash projection

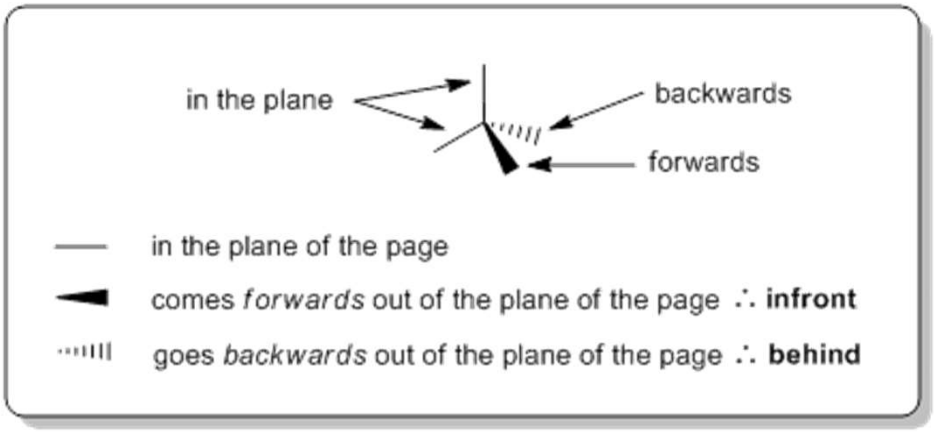
- The Flying-Wedge projection is the most common three-dimensional representation of a three dimensional molecule on a two dimensional surface (paper)
- This kind of representation is usually done for molecules containing chiral centre. In this representation, the ***ordinary lines represent bonds in the plane of the paper***. A solid Wedge (◀) represents a **bond above the plane of the paper** and a dashed wedge (|||) or a broken line represents a **bond below the plane of the paper.**



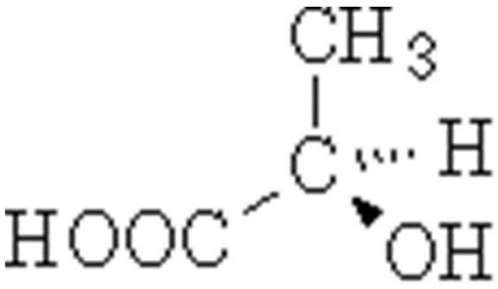
Methane



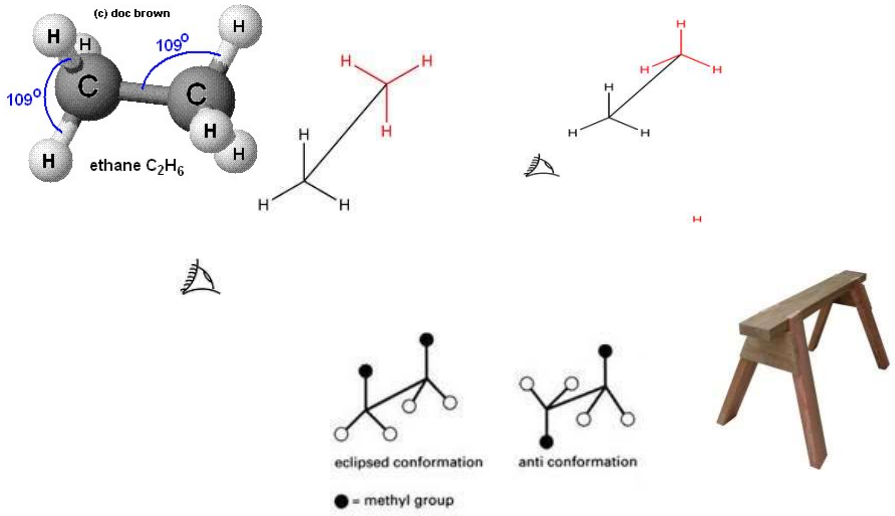
Wedge – Dash projection



The Flying-Wedge projection formula of Lactic acid $CH_3CH(OH)COOH$ for example, can be shown as follows…..



Sawhorse projection

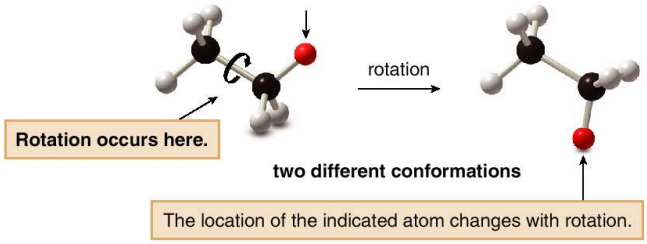


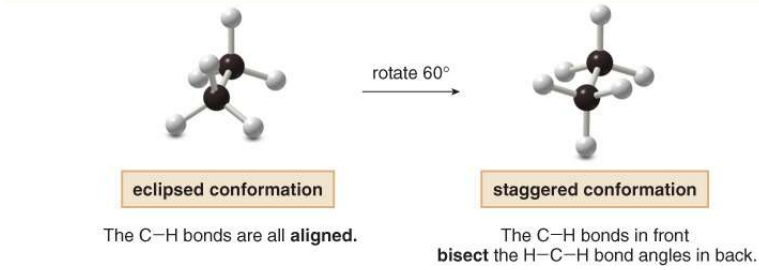
Sawhorse projection

- In this representation, the molecule is **viewed slightly from above** and form the right and then projected on the paper
- The bond between the two carbon atoms **is drawn diagonally** and of a relatively greater length for the sake of clarity
- The **lower left hand carbon is taken as the front carbon** and the **upper right hand carbon as the back carbon**
- All **parallel bonds in sawhorse formula are eclipsed** and **all anti parallel bonds are opposite** or **trans/anti** to each other
- The sawhorse presentation of **eclipsed and staggered conformations** of ethane was shown in the previous slide

Conformations of acyclic alkanes

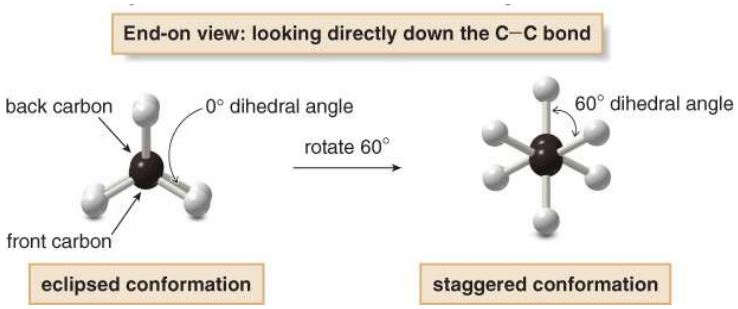
Conformations are different arrangements of atoms that are interconverted by **rotation about single bonds**



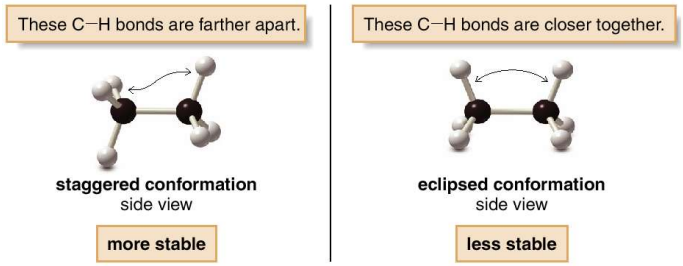


- Names are given to two different conformations
- In the **eclipsed conformation**, the C—H bonds on one carbon are **directly aligned** with the C—H bonds on the adjacent carbon
- In the **staggered conformation**, the C—H bonds on one carbon **bisect** the H—C—H bond angle on the adjacent carbon

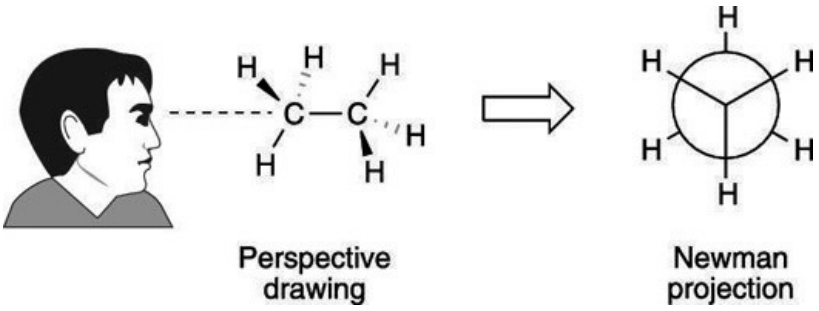
- Rotating the atoms on one carbon by 60° converts an eclipsed conformation into a staggered conformation, and vice versa.
- The angle that separates a bond on one atom from a bond on an adjacent atom is called a **dihedral angle**. For ethane in the staggered conformation, the **dihedral angle for the C—H bonds is 60°. For eclipsed ethane, it is 0°.**



- The staggered and eclipsed conformations of ethane **interconvert** at room temperature, **but each conformer is not equally stable**
- The **staggered conformations are more stable** (lower in energy) than the eclipsed conformations
- **Electron-electron repulsion between bonds** in the eclipsed conformation increases its energy compared with the staggered conformation, where the bonding electrons are farther apart



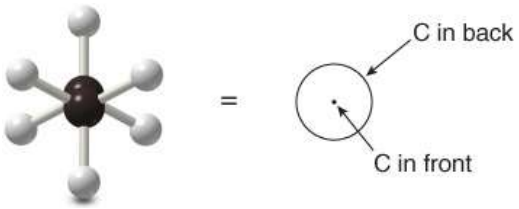
Newman projection



- End-on representations for conformations are commonly drawn using a convention called a Newman projection.

How to Draw a Newman Projection:

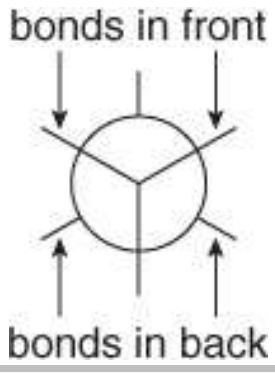
Step 1. Look directly down the C—C bond (end-on), and draw a circle with a dot in the center to represent the carbons of the C—C bond.



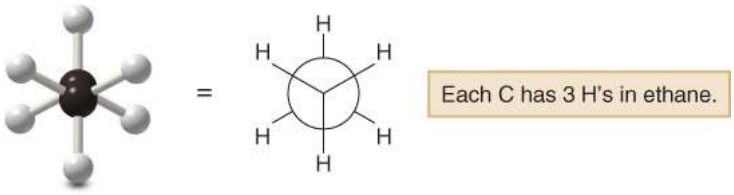
Step 2. Draw in the bonds.

Draw the bonds on the front C as **three lines meeting at the center of the circle.**

Draw the bonds on the back C as **three lines coming out of the edge of the circle.**

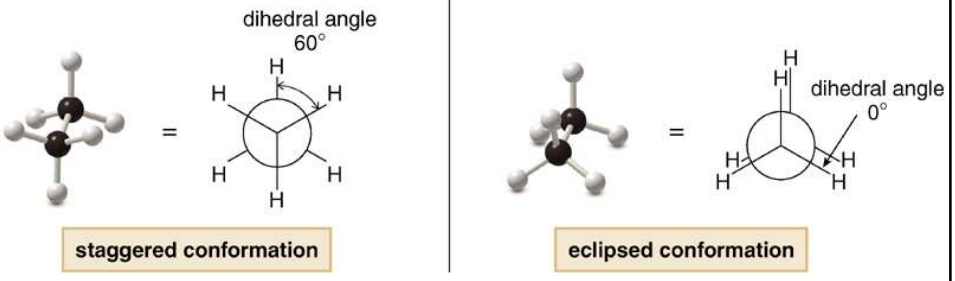


Step 3. Add the atoms on each bond.

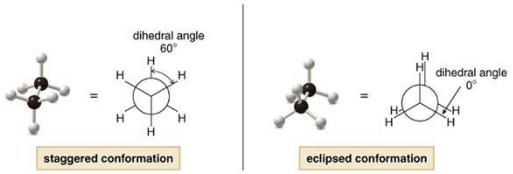


Each C has 3 H's in ethane.

Newman projection

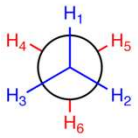


- In the **staggered form**, all the bonds attached to the C1 and C2 carbon atoms are **maximum apart from each other** whereas in the **eclipsed form**, the bonds attached to the two carbon atoms are **closest to each other**.

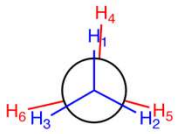


- Energetically, out of the two forms, the **staggered form is the more favored form** - bonds are maximally apart from each other – hence has the **least amount of stearic strain**
- On the other hand, the bonds are closest to each other in the eclipsed form and it **has the highest energy**
- The strain existing in the eclipsed form is termed as **torsional strain (resistance to bond twisting).** The energy barrier between the two forms in the ethane molecule has been experimentally found to be about 3 kcal/mol

- 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**.



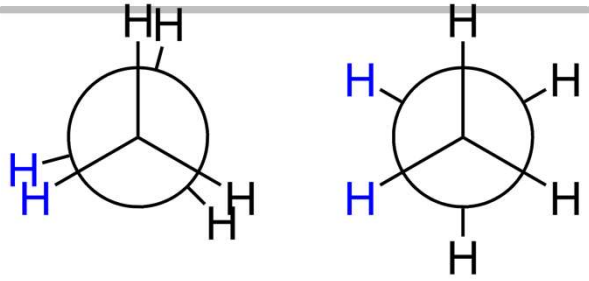
1



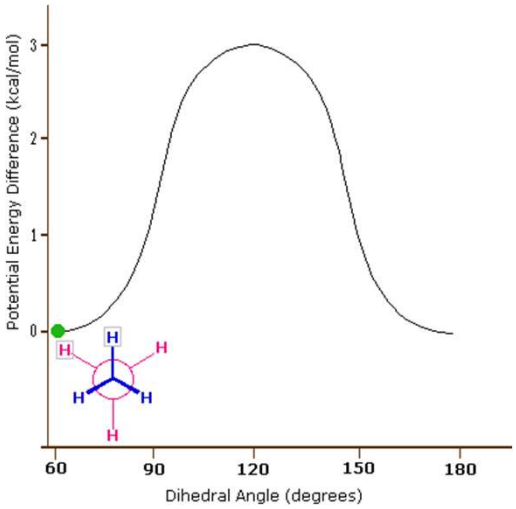
2

- **The smallest dihedral angle is 60º in 1; it is 0º in 2**. Thus, two C-H bonds not sharing a carbon atom that are closest to each other **(ex: C-H1 and C-H4) are closer in 2 than in 1.**
- The repulsion between electrons in bonds that do not share a carbon atom is, therefore, greater in 2 than in 1. **Consequently, torsional strain is greater in 2 than in 1.**

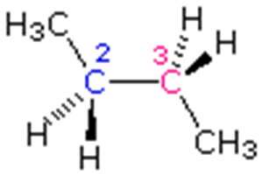
Newman projection



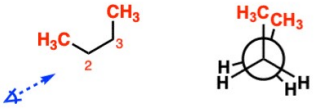
- In these Formulae the **molecule is viewed from the front.** The carbon atom **nearer to the eye is represented by a point** and the three atoms or groups are shown attached to it by **three lines at an angle of 120^0** to each other.
- A **Newman Projection** can be drawn such that the groups on the front carbon are *staggered* (60 degrees apart) or *eclipsed* (directly overlapping) with the groups on the back carbon. Below are two **Newman Projections** of ethane, C_2H_6. The structure on the right is staggered, and the structure on the left is eclipsed.



Newman projection, n-butane



Eclipsed



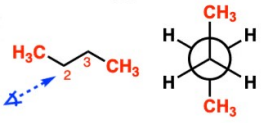
Highest-energy conformation of butane

Front groups **eclipsed** with respect to back groups

CH_3 groups are ***syn*** (dihedral angle 0°)

Strain energy about **5.0 kcal/mol** above that of the staggered conformation (at right)

Staggered



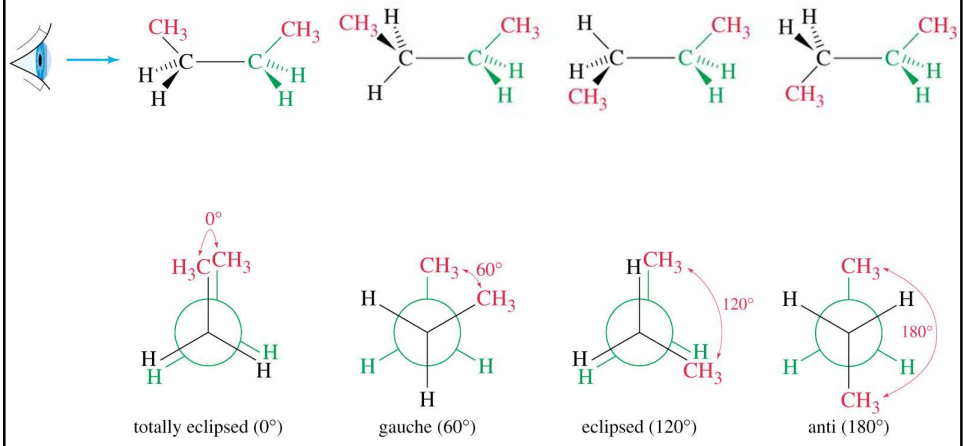
Lowest energy conformation of butane

Front groups **staggered** with respect to back groups

CH_3 groups are ***anti*** (dihedral angle 180°)

Energy minimum

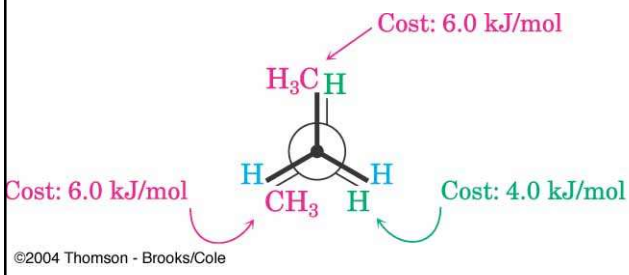
n - butane conformations (C_2-C_3)



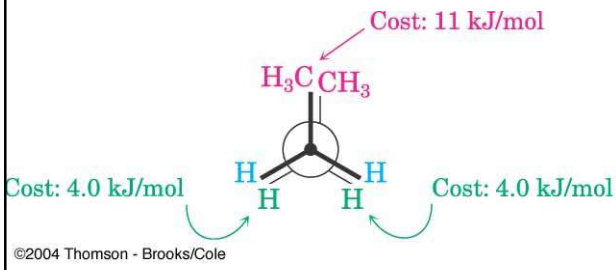
Definitions

- **Anti** - Description given to **two substituents attached to adjacent atoms when their bonds are at 180°** with respect to each other
- **Syn** - Description given to **two substituents attached to adjacent atoms when their bonds are at 0°** with respect to each other
- **Gauche** - Description given to **two substituents attached to adjacent atoms when their bonds are at 60°** with respect to each other

Two Different Eclipsed Conformations



Total cost: 16 kJ/mol



Total cost: 19 kJ/mol

Strain energy can be quantified

TABLE 4.1 Energy Costs for Interactions in Alkane Conformers

Interaction	Cause	Energy cost (kJ/mol)	Energy cost (kcal/mol)
H ↔ H eclipsed	Torsional strain	4.0	1.0
H ↔ CH_3 eclipsed	Mostly torsional strain	6.0	1.4
CH_3 ↔ CH_3 eclipsed	Torsional plus steric strain	11.0	2.6
CH_3 ↔ CH_3 gauche	Steric strain	3.8	0.9

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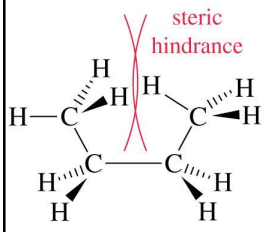
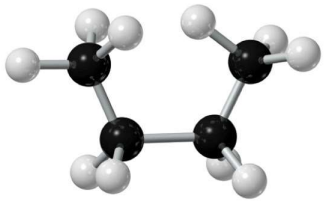
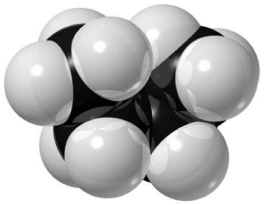
Steric and Torsional Strain both when Eclipsed

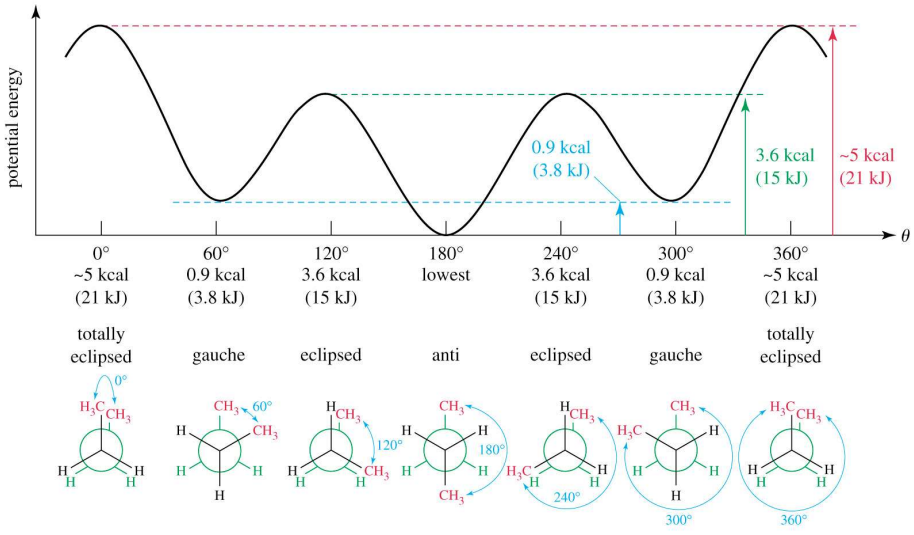






Totally eclipsed conformation of butane

PE Diagram for Butane



- There are **two energy minima, the *gauche* and *anti* forms**, which are both **staggered** and thus have no **torsional strain**
- The ***anti* form is the absolute energy minimum**, since the *gauche* form has a small steric interaction between the two methyl groups. At a dihedral angle of 60 degrees, one hydrogen of each of the methyl groups is relatively close to a hydrogen of the other methyl group (van der Waals repulsion)
- Carefully note the difference between **steric strain** and **torsional strain**. The latter arises from eclipsed bonds, while the former arises from atoms which are too close to each other

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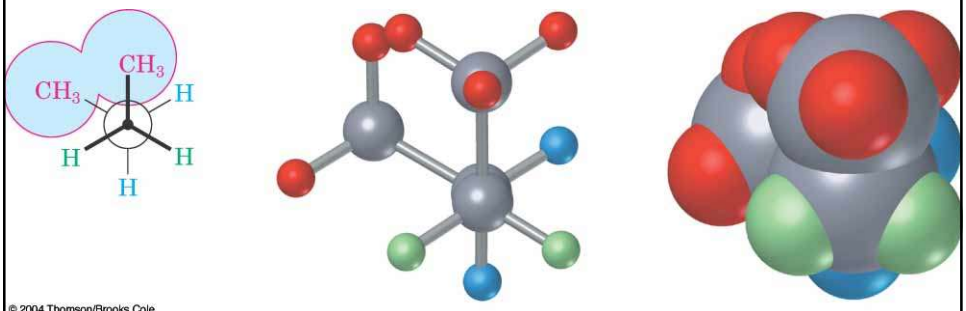
Gauche Interaction in Butane



- There are **also two energy maxima, both of which are eclipsed and thus torsionally strained**. The higher energy conformation also has steric strain

- ***Torsional strain* arises from the repulsion of electrons in bonds; *steric strain* arises from atoms that are too close!**

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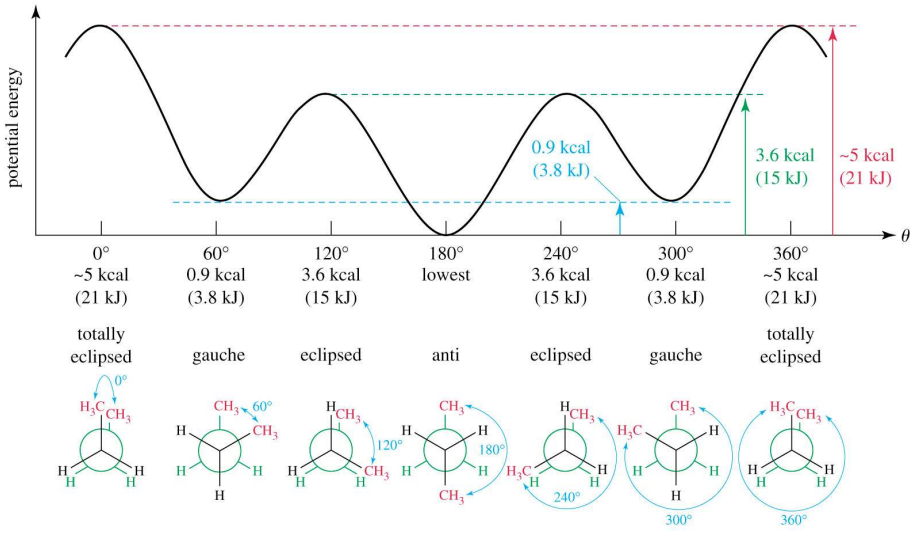
PE Diagram for Butane



Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.