

Structure and Stereochemistry of Alkanes

Reading: Wade chapter 3, sections 3-1- 3-9

Study Problems: 3-33, 3-37, 3-39, 3-40, 3-42

Key Concepts and Skills:

- Explain and predict trends in the physical properties of alkanes
- Correctly name alkanes, and given a name, draw the structure and give the molecular formula.
- Compare the energies of alkane conformations and predict the most stable conformation

Lecture Topics:

I. Alkanes, formula and nomenclature

Alkanes are hydrocarbons consisting of C-C and C-H single bonds. These compounds are said to be **saturated**, that is, each carbon has the maximum possible number of hydrogens bound.

Molecular formula: C_nH_{2n+2} – a general formula for branched and unbranched hydrocarbons. Consider the constitutional (structural) isomers pentane, isopentane and neopentane

An alkane **homolog** differs only in the number of CH_2 groups.

Example: butane: $CH_3CH_2CH_2CH_3$ and pentane $CH_3CH_2CH_2CH_2CH_3$ are homologs.

Nomenclature The simple alkanes which are unbranched are termed n-alkanes (normal alkanes): example: n-butane, n-pentane, n-hexane, etc.

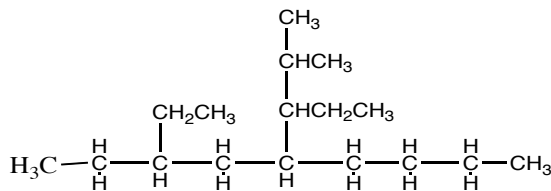
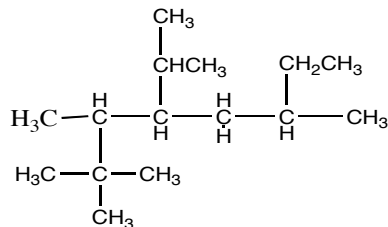
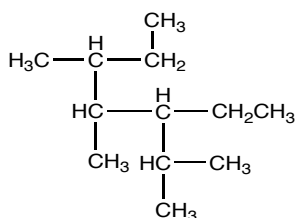
IUPAC has established rules for the nomenclature of organic compounds:

1. Find the longest continuous chain of carbon atoms and use the name of this chain as the base name. When there is a choice between two equal length chains, use the one with the most substituents. **Substituents** are alkyl groups attached to the main chain.
2. Number the longest chain beginning with the end of the chain nearest a substituent.
3. Name the substituents attached to the longest chain as alkyl groups. Give the location of each alkyl group by the number of the main chain carbon it is attached to.
 - a. methyl group: CH_3-
 - b. ethyl group: CH_3CH_2-
 - c. n-propyl: $CH_3CH_2CH_2-$
 - d. isopropyl: $(CH_3)_2CH-$
 - e. n-butyl: $CH_3CH_2CH_2CH_2-$
 - f. isobutyl: $(CH_3)_2CHCH_2-$
 - g. sec-butyl: $CH_3CH_2CH(CH_3)-$
 - h. tert-butyl: $(CH_3)_3C-$

Halogen groups are named as fluoro, chloro, bromo, iodo.

- When two or more substituents are present, list them in alphabetical order. When two or more of the same alkyl substituents are present, use prefixes di-, tri-, tetra-, penta-, hexa- etc.
- Complex alkyl groups are named as above using the “head carbon” bonded to the main alkyl chain as carbon #1.

Example: Name the following structures



II. Solubilities, Melting points, Boiling Points of alkanes

Alkanes are **hydrophobic** and are insoluble in water but soluble in weakly polar organic solvents.

The **boiling points** of alkanes increase with increasing molecular weight. Branched alkanes boil at lower temperatures than n-alkanes with the same number of carbon atoms. Branched alkanes have less surface area for London forces.

Alkane Melting points increase with increasing molecular weight:

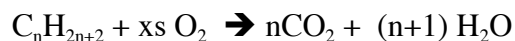
- Alkanes with odd numbers of carbon atoms do not pack as well, and they melt at lower temperatures.

- Alkanes with even numbers of carbon atoms pack better into a solid structure, so a higher temperature is required to melt them.

- Branching of an alkane gives it a more compact structure that packs more easily into a solid and increases the melting point

III. Reactions of Alkanes

a. Combustion is the rapid oxidation of alkanes that takes place at high temperatures



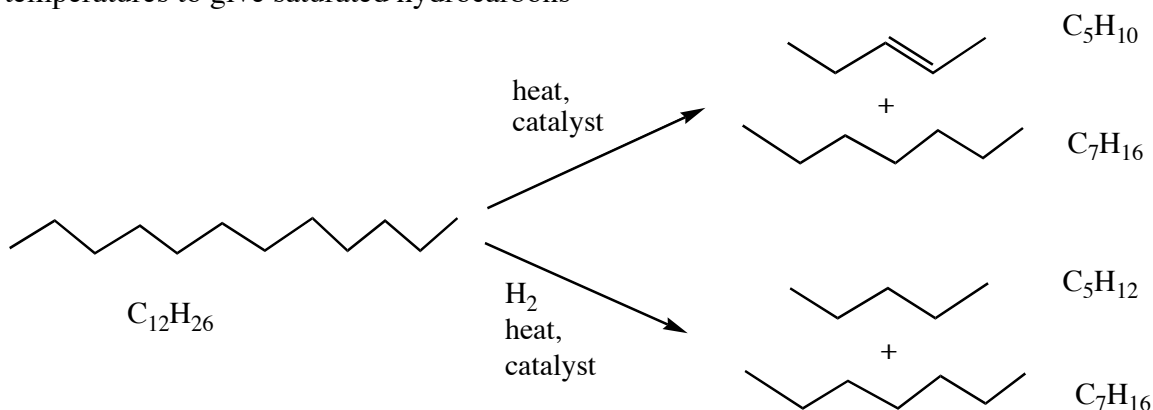
Ex.:



difficult to control.

b. High-temperature **Cracking** of hydrocarbons produces smaller hydrocarbons that are mixtures of alkanes and alkenes

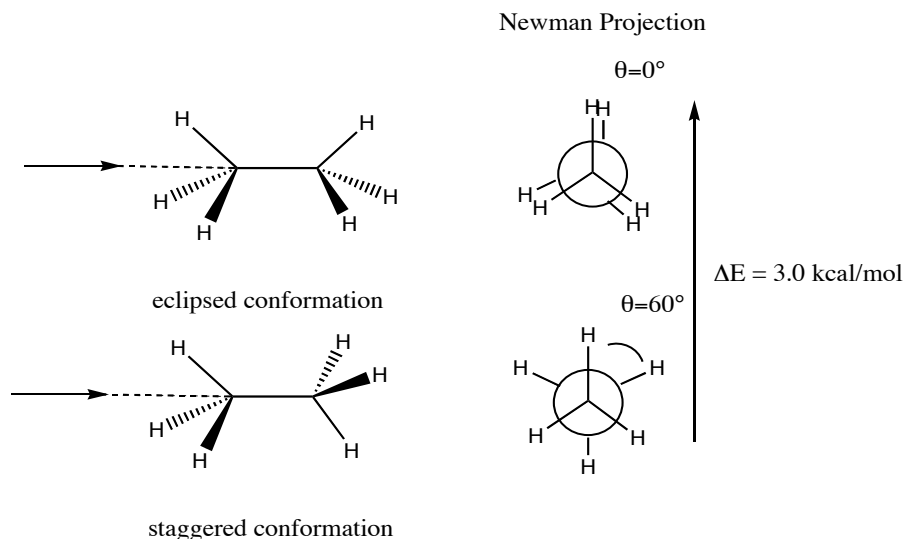
c. In **Hydrocracking**, hydrogen gas is added to hydrocarbons at elevated temperatures to give saturated hydrocarbons



d. Alkanes can react with halogens (Cl_2 , Br_2 , F_2 , I_2) in the presence of heat or light as an initiator to form alkyl halides.

IV. Structure and Conformation of Alkanes

Ethane has two methyl groups joined by a sigma bond; free rotation about the sigma bond is observed. In drawing **conformers** or **conformations** of molecules, use **Newman projections**, which are a way of drawing a molecule looking down the bond connecting two C atoms. Ethane has two major conformations, staggered and eclipsed; the eclipsed form is 3 kcal/mol higher in energy than the staggered form.

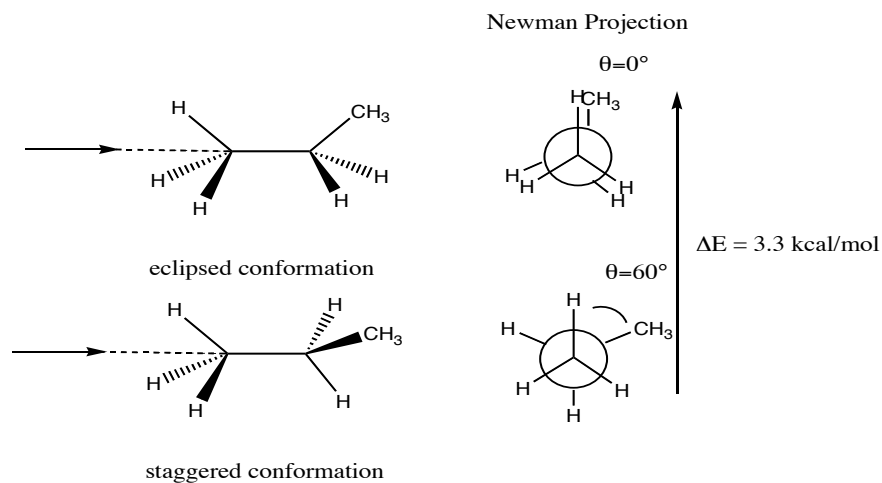


The **dihedral angle** (θ) is the angle between the CH bond on the front carbon and the CH bond on the back carbon. As ethane rotates toward the eclipsed conformation, there is a resistance to rotation called **torsional strain**. The **torsional energy** barrier that must be overcome is 3.0 kcal/mol. Thermal energies allow sampling of all possible conformers, but at any given time there will be a greater population in the staggered conformation, in

which the CH bonds are separated as much as possible (which avoids repulsion of the electron clouds in the CH bonds in the eclipsed form).

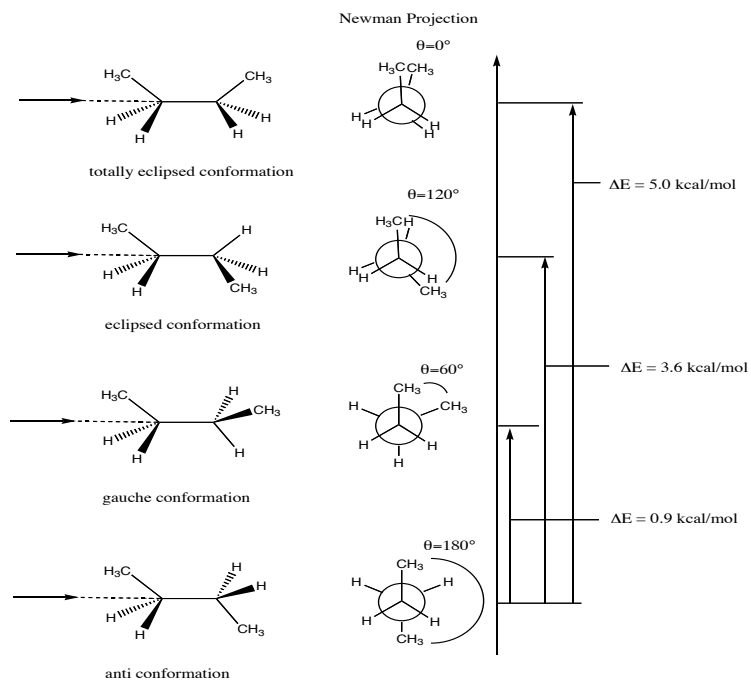
Conformational analysis is the study of the energetics of different conformations.

For **Propane**, the eclipsed form is 3.3 kcal/mol higher in energy than the staggered form:

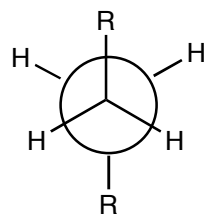
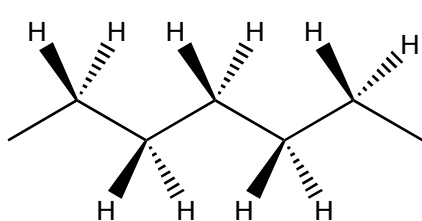


Conformations of Butane

There are several conformations of butane. The **totally eclipsed** conformer is 5 kcal/mol higher in energy than the anti conformer; the eclipsed conformer is 3.6 kcal/mol higher in energy than the anti conformer, and the gauche conformer is 0.9 kcal/mol higher in energy than the anti conformer. When the two end methyl groups are forced together, the electron-cloud repulsion generates **steric strain** or **steric hindrance** to rotation. C-C single bonds will assume a staggered or anti conformation whenever possible to avoid eclipsing interactions and steric strain.



Thus, the most stable arrangement for alkanes is a zig-zag structure in which each carbon in the chain heavily populates the anti conformer.

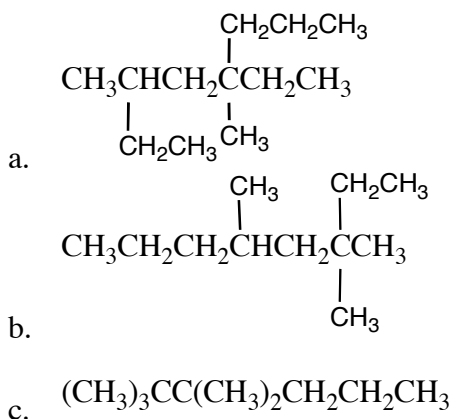


R=alkyl group

anti conformation

Additional Problems for practice:

1. Draw a graph of potential energy versus dihedral angle for each of the following rotations. Draw a Newman projection for each staggered and eclipsed conformation.
 - a. rotation about the C2-C3 bond of 2-methylbutane
 - b. rotation about the C2-C3 bond of 2,3-dimethylbutane
2. Supply proper IUPAC names for the following compounds. Indicate the degree of substitution at each carbon (1° , 2° , 3° , 4°)



3. Order the following compounds with respect to their boiling points, from least to greatest. Do the same for their melting points.

