

CHEM 321 Organic Chemistry - Professor Kathleen V. Kilway
"Organic Chemistry" by Maitland Jones, 3rd edition

Homework problems for Chapter 2 - 1, 4, 5, 8, 9, 11, 14, 16, 22, 23, 24, 25, 27, 33, 35, 38, 40, 41, 43, 48, 50, 51, 53, 54, 55.

CHAPTER 2: ALKANES

Section 2.1

I. Preview

Section 2.2

II. Hybrid Orbitals: Making a Model For Methane

A- Hybridization

- 1- This is a mathematical model in which atomic orbital wave functions are combined to make new hybrid orbitals.
- 2- Combination of the four atomic orbitals of carbon ($2s$, $2p_x$, $2p_y$, $2p_z$) to produce four new orbitals, called hybrid orbitals.
- 3- The four hybrid orbitals overlap with the $1s$ orbitals of four hydrogens to produce methane.

B- sp Hybridization

- 1- Combination of one s and one p orbital.
- 2- See Figure 2.3 on page 50 for a good example.
- 3- The two orbitals can be combined in a constructive ($2p+2s$), called bonding, or a deconstructive ($2p-2s$), called antibonding, way.

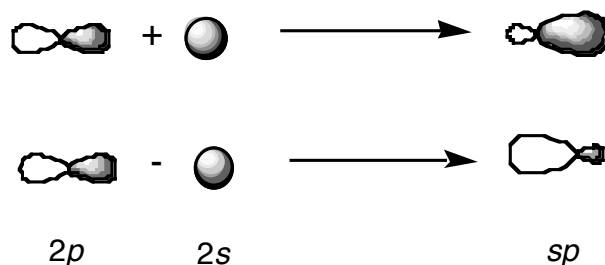


Figure 1

- 4- The new orbitals in Figure 2.3 have no longer equally sized lobes and are now called hybrid orbitals.
 - a- This means that 50% of the orbitals are s and 50% are p .
 - b- Overlap of the orbitals is increased.
 - i- See Figure 2.4 on page 50.
 - ii- The better the overlap the greater the stability and the stronger the bond.
 - c- They are aimed 180 degrees from one another.
- 5- An example of sp hybridization is BeH_2 .
 - a- Valence electrons on Be are $2s^2$.

- b- Construct sp hybrids from one Be $2s$ atomic orbital and one of Be's three empty, equivalent $2p$ orbitals.
- c- For one bond, one sp orbital of the Be and one s orbital of the H is used.
- d- Overall bonding interaction.
- e- This is consistent with the Lewis dot structure (See Figure 2).



Figure 2

- f- The combination of Be (sp) and H ($1s$) orbitals must also yield an antibonding orbital ($sp-1s$).
 - i- See Figure 2.5 on page 51 for an example.
- 6- Sigma Bonds (σ)
 - 1- This is any bond that has cylindrical symmetry.

C- sp^2 Hybridization

- 1- They are made from one s orbital and two p orbitals.
- 2- 33% = s & 67% = p .
- 3- See Figure 2.6 on page 53 for top and side views of this hybrid.
- 4- Bonding is in the plane on the indices of a triangle (120 degrees).
- 5- An example of sp^2 hybridization is BH_3 .

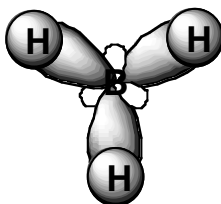


Figure 3

D- sp^3 Hybridization: Methane

- 1- They are made from one s orbital and three p orbitals.
- 2- 25% = s , 75% = p .
- 3- The carbon in methane is sp^3 hybridized.
- 4- See Figure 2.7 on page 53 for the proper molecular arrangement of methane.
- 5- Resulting orbitals are 109.5 degrees apart and pointed toward the corners of a tetrahedron.

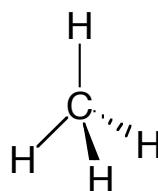
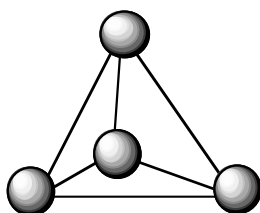


Figure 4

For a Quicktime movie from Professor Kent Wilson's group showing *s* and *p* orbitals regarding elements click here:

<http://www-wilson.ucsd.edu/education/gchem/molecorbs/QuickTime/molorbs.qt>

E- Why Hybridization

- 1- See Figure 2.9 on page 55 for a first approximation of the structure of methane.
- 2- Three flaws of proposed model.
 - a- The electrons in the bonds are far from being as remote from each other as possible.
 - b- Two electrons occupy a nonbonding orbital and, therefore, don't contribute to holding the molecule together (See Figure 2.10 on page 55).
 - c- Bonds are formed through overlap between carbon *2p* and hydrogen *1s* orbitals, thus wasting the rear lobes of the *2p* orbitals.
- 3- The hybridization model solves all the above flaws.
 - a- The four hybrid orbitals are directed toward the corners of a tetrahedron.
 - b- All electrons are in bonding orbitals.
 - c- Overlap is improved in the bonds using the fat lobes of the hybrid *sp*³ orbitals and hydrogen *1s* orbitals.
- 4- Table 2.1 on page 57 gives a review of *sp*, *sp*² and *sp*³ hybrid orbitals.

Section 2.3

III. Derivatives of Methane: Methyl (CH₃) and Methyl Compounds (CH₃X)

A- Methyl Compounds

- 1- These are considered derivatives of methane.
- 2- Their names are formed by dropping the "ane" from the original methane group.
- 3- Then appending it with "yl."

B- Alkyl

- 1- This is just a general term used for alkane derivatives.
- 2- A general abbreviation for this group is R-X.
- 3- See Table 2.2 on page 59 for some general derivatives of methane.

Section 2.4

IV. The Methyl Cation (⁺CH₃), Anion (⁻:CH₃), and Radical ([•]CH₃)

A- Reactive Intermediates

- 1- These are types of compounds that are too unstable to be isolated under normal conditions.
- 2- Good examples are the methyl cation, the methyl anion and the methyl radical.
- 3- See Figures 2.17, 2.18 & 2.19 on pages 61 and 62 for examples.

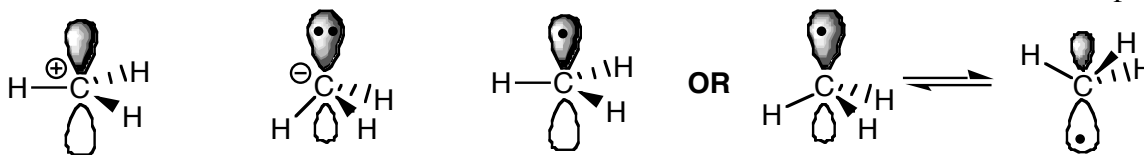


Figure 5

Section 2.5

V. Ethane (C_2H_6), Ethyl Compounds (C_2H_5X), and Newman Projections

A- Ethane

- 1- This is the second member of the alkane class.
- 2- See Figure 2.20 on page 63 for the structure of ethane.

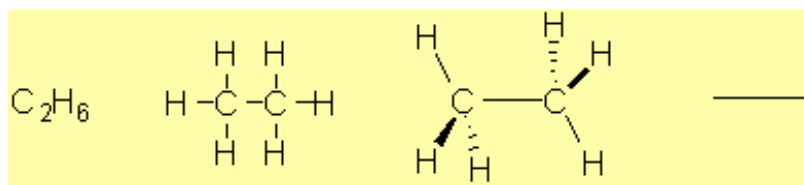


Figure 6

3- Structural Questions

- a- From Figure 2.21 we see that looking at one carbon the methyl group takes up more room than the hydrogens.
 - i- So the H_3C-C-H angle is bigger than the $H-C-H$ angle.
 - ii- $H_3C-C-H = 111.0$ degrees & $H-C-H = 109.3$ degrees.
- b- Conformations
 - i- They are 3-D molecular structures that are related by the rotations about bonds.
 - ii- Ethane has two conformations.
 - iii- See Figure 2.22 on page 64 for the two conformations of ethane.
- c- Eclipsed Ethane
 - i- This is where all the carbon-hydrogen bonds are as close as possible (the hydrogens from one methyl are directly in front of the hydrogens from the other methyl).
 - ii- Not an energy minimum.
 - iii- **Transition state** - top of a barrier separating two other forms (See Figure 7).

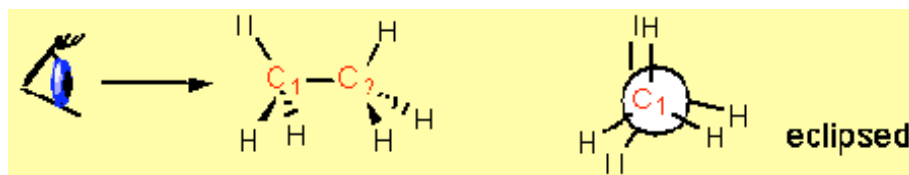


Figure 7

d- Staggered Ethane

- i- This is where the carbon-hydrogen bonds are as far apart as possible.
- ii- Energy minimum (See Figure 8).

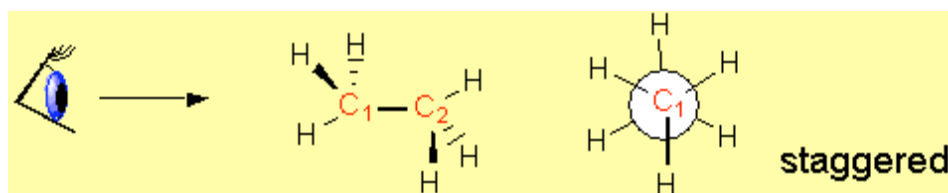


Figure 8

e- An effective way of viewing these structures is called Newman Projections.

- i- See Figure 2.23 on page 65 for an example.
- f- Plot of dihedral angle as a function of energy.
 - i- **Dihedral angle** - is the torsional, or twist, angle between H-C-C and C-C-H planes.
 - ii- See Figure 9 below and Figure 2.24 on page 66.
 - iii- Torsional strain - 1 kcal/mol for each pair of eclipsed carbon-hydrogen bonds.
 - iv- Ethane has a torsional strain of 3 kcal/mol.

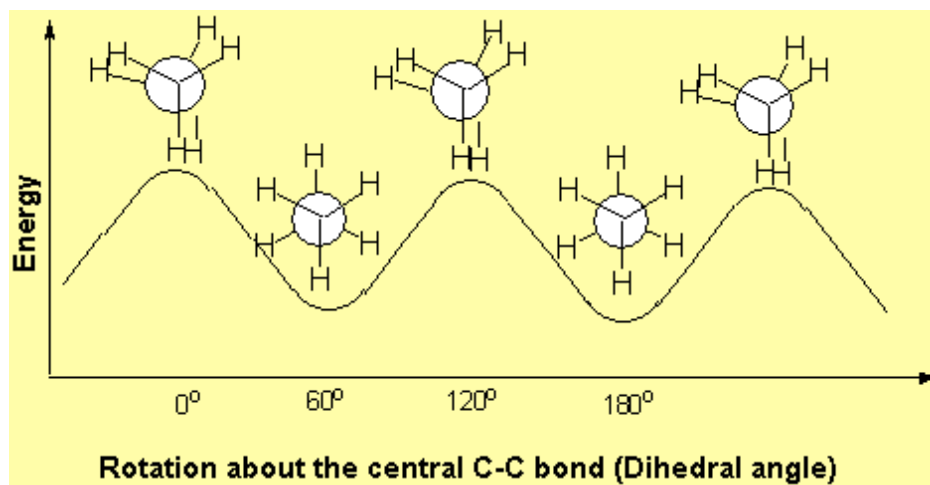


Figure 9

For a Quicktime movie of the Conformation of Ethane click here:

<http://slater.cem.msu.edu:80/~parrill/movies/conf.html>

<http://slater.cem.msu.edu:80/~parrill/movies/ethaneneuman.mov>

B- Ethyl Compounds

- 1- Table 2.3 on page 68 gives some examples of ethyl compounds.

Section 2.6**VI. Structure Drawings**

Section 2.7

VII. Propane (C_3H_8) and Propyl Compounds (C_3H_7X)

A- Propane

- 1- This is the third member of the alkane series.
- 2- See Figure 2.29 on page 71 for several representations of propane.

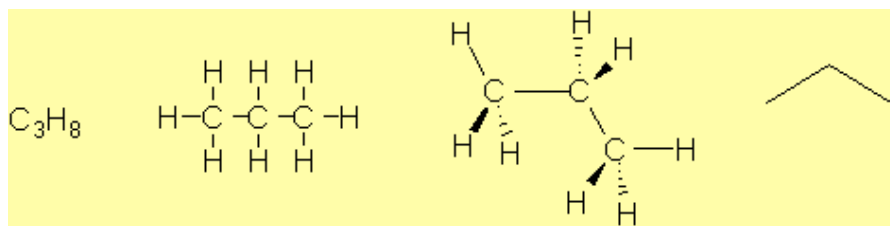


Figure 10

B- Methylene Group

- 1- This is the central $-CH_2-$ group.

C- Propyl Compounds

- 1- The linear compound $CH_3-CH_2-CH_2-X$ is called propyl-X.
- 2- The branched compound $CH_3-CHX-CH_3$ is called isopropyl-X.
- 3- See Figure 2.32 on page 72 for an example.

Section 2.8

VIII. Butanes (C_4H_{10}), Butyl Compounds (C_4H_9X), and Conformational Analysis

A- Butane

- 1- This is the fourth member in the straight-chained alkanes.
- 2- See Figure 11 below and Figure 2.34 on page 73 for different representations of butane.

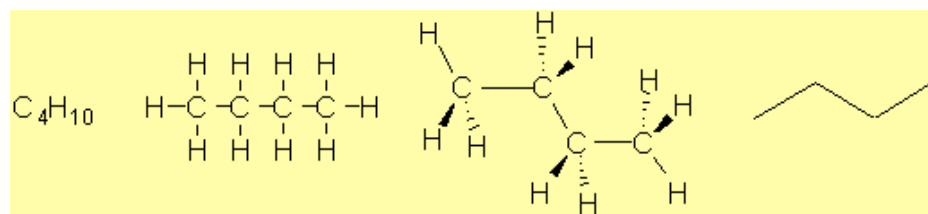


Figure 11

- 3- See Table 2.4 on page 73 for a list of straight-chained alkanes.
- 4- Conformational Analysis
 - a- Butane is a good example.
 - b- This is the study of relative energies of conformational isomers.
 - i- Conformations looking down $C(2)-C(3)$ bond of butane (See Figure 2.35 on page 74 for an example).
 - a- anti form: staggered, methyl groups opposite.
 - b- gauche form: staggered, methyl groups adjacent.

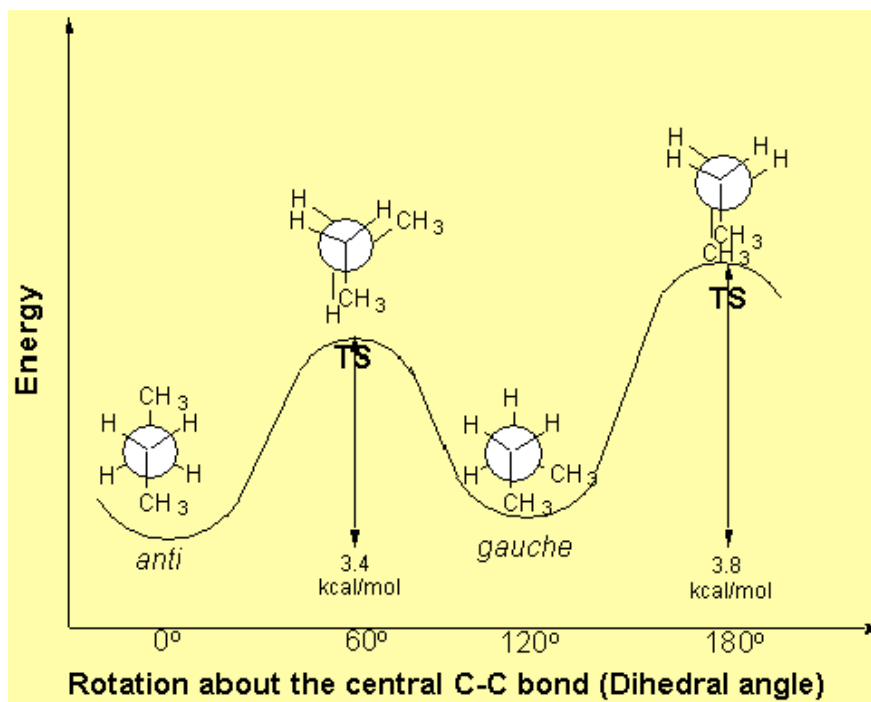


Figure 12

For movies of butane rotation, check out:

<http://slater.cem.msu.edu:80/~parrill/movies/butane.mov>

<http://slater.cem.msu.edu:80/~parrill/movies/butanenewman.mov>

B- 4 Derivatives of C_4H_9-X

- 1- Butyl.
- 2- Isobutyl.
- 3- *Sec*-Butyl.
- 4- *Tert*-Butyl.
- 5- See Figure 2.36 and 2.37 on pages 75 and 76 for representations of these derivatives.

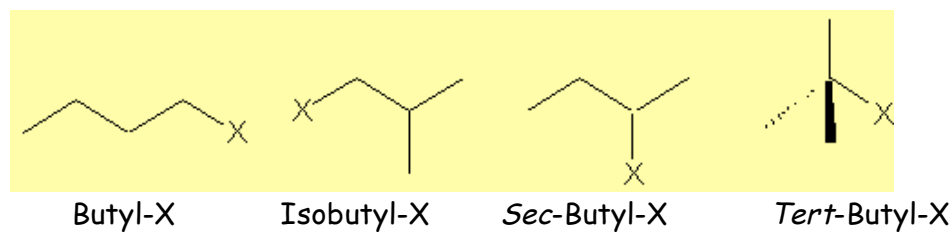


Figure 13

Section 2.9

IX. Pentanes (C_5H_{12}) and Pentyl Compounds ($C_5H_{11}X$)

A- Pentane

- 1- The fifth member of the alkane class.
- 2- There are three different pentanes.
 - a- Pentane.

- b- Isopentane.
 - i- IUPAC name = 2-methylbutane
 - c- Neopentane.
 - i- IUPAC name = 2,2-dimethylpropane
- 3- See Figure 2.38 on page 76 for a visual representation of all pentanes.

B- Pentyl Derivatives

- 1- See Figure 2.41 on page 78 for examples of pentyl derivatives.

Section 2.10

X. The naming Conventions for Alkanes

A- Steps

- 1- Look for the longest straight chain of carbons.
 - a- An easy way to determine the longest chain is by taking your pencil and following along the carbons.
 - b- Try several different routes. Then count the carbons.
 - c- The chain is numbered from the end, which has the lowest position number for the substituents.
- 2- The substituent is numbered based on the position of the parent hydrocarbon.
 - a- So that it produces the lowest number for the substituent.
- 3- All substituents receive numbers.
 - a- If the substituents are identical use the prefixes di-, tri-, etc....
 - b- If they are not identical place them in alphabetical order.
- 4- When you cannot determine the order just start with the lowest number.
- 5- Additional handout is also helpful.

Section 2.11

XI. Problem Solving: Writing Isomers

A- Steps

- 1- Begin with the longest chain possible.
- 2- Start on the left side of the chain and shorten the chain by one carbon.
 - a- Then add the extra carbon as a methyl group.
 - b- Move this carbon to all possible positions.
- 3- Once again shorten the chain by one carbon.
 - a- Add the extra carbons as two methyl groups or as one ethyl group.
 - b- Move the carbons to all possible positions.
- 4- Shorten the chain again.
 - a- Repeat steps again.
- 5- Try to be systematic. It takes practise.

Section 2.12

XII. Rings

A- Saturated Alkanes

- 1- They have the molecular formula of C_nH_{2n+2} .

B- Unsaturated Alkanes

- 1- They have the molecular formula of C_nH_{2n} .
- 2- Rings are examples of unsaturated alkanes.

C- Naming

- 1- Ring compounds are named by adding the prefix cyclo- to the parent hydrocarbon.
- 2- See Figure 2.52 on page 83 for the formation of cyclopentane.

D- Sidedness

- 1- *cis*- This occurs when both methyl groups are positioned on the same side of the ring.
- 2- *trans*- This occurs when the methyl groups are on the opposite sides of the ring.
- 3- See Figure 2.54 on page 84 for examples of *cis* and *trans*.

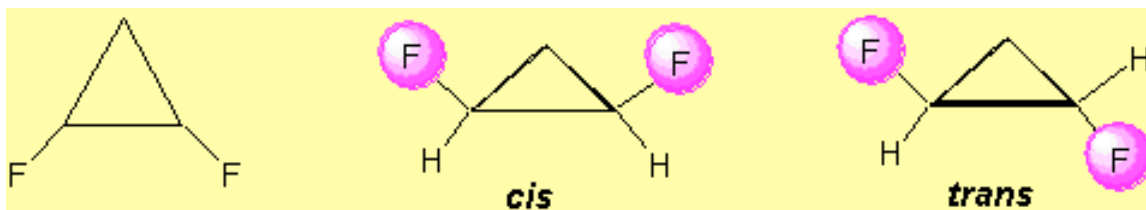


Figure 14

Section 2.13**XIII. Physical Properties of Alkanes and Cycloalkanes****A- van der Waals forces**

- 1- These are intermolecular forces in molecules.
- 2- They are caused by induced dipole-induced interactions.

Section 2.14**XIV. Nuclear Magnetic Resonance Spectroscopy**

- 1- Study of molecules through the investigation of their interactions with electromagnetic radiation.
- 2- Every different carbon (or hydrogen) in a different environment gives a different signal from that of the other carbons (or hydrogens) in the molecule.
- 3- See Figure 2.59 on page 89 for an example.

Section 2.15**XV. Acids and Bases Revisited: More Chemical Reactions****A- Lewis Definition**

- 1- Any reaction between a reactive pair of electrons in a filled orbital and an empty orbital is an acid-base reaction.
 - a- Lewis Acid: empty orbital.
 - b- Lewis Base: filled orbital.

2- See Figure 2.62 on page 91 for an example.

B- Arrow Formalism

1- Show the electron flow as the new bond is formed.

2- See Figure 2.64 on page 91 for an example.