Chapter 2 – Alkanes

Introduction

One of the major challenges in learning organic chemistry is to see beyond the information in a structural formula. You already got a small taste of this in the previous chapter when you learned how to predict bond angles, locate partial charges (polar bonds), and adjust bonding and charge patterns associated with delocalized electrons (resonance hybrids). Each of these attributes required you to go "beyond the formula" and add more information.

This chapter adds several new types of "beyond formula" information:

1. **Conformation.** Most organic molecules are flexible and can quickly flip through a variety of shapes called *conformations*. This chapter shows you how to predict which alkanes are flexible and which are not. It also shows you how to predict the most stable (popular) conformations of flexible alkanes.
2. **Physical properties.** Boiling temperature, melting temperature, solubility – all of these things somehow depend on the combinations of atoms that a molecule contains. This chapter introduces some of the principles that connect structure with properties.
3. **Molecular energy.** The two most important things that an organic chemist needs to know about a molecule are its *structure* and its *energy*. Being able to look at two molecular formulas (or models) and think clearly about their relative energies may be the Holy Grail of Chem 201. This chapter introduces two *destabilizing factors* that appear throughout this course: *torsional strain* (p. 51) and *van der Waals repulsion* (p. 55).

Notice that each of these characteristics is rooted in a molecule's structure, but is never drawn in a structural formula. Therefore, your task is 1) to learn how to add this information to any formula, and 2) be prepared to do this with every formula you meet.

Checklist

When you have finished studying Chapter 2, you should be able to:

1. Recognize and name molecules, and groups inside molecules, that are
    a. members of the following *families* of compounds: *hydrocarbons, aliphatic hydrocarbons vs. aromatic hydrocarbons* (that include a benzene ring), *alkanes (n-alkanes vs. branched alkanes), alkenes, alkynes, cycloalkanes*
    b. *n*-alkanes containing from one to twelve carbons (Table 2.1)
    c. all *alkyl substituents*, unbranched and branched, containing from one to five carbons (Table 2.2)
    d. alkanes and cycloalkanes that can be named by combining the groups that appear in items #2b and #2c
    e. *methylene* groups
    f. R-, Ph-, Ar- *substituents*
2. Recognize and draw structural formulas for the following structural units:
    a. *primary, secondary, tertiary,* and *quaternary* carbon and hydrogen atoms
    b. O-containing functional groups: *alcohols, carboxylic acids, ethers*
    c. N-containing functional groups: *amines, nitriles, amides*
3. Draw and interpret
    a. *condensed* formulas of alkanes
    b. *skeletal formulas*
4. Recognize and draw *constitutional isomers*
5. Identify alkanes that are likely to exist as a mixture of *conformational isomers* and describe the conformational changes needed to interconvert these isomers by
    a. drawing *Newman projections* of all conformational isomers produced by rotation about a selected bond
    b. drawing an energy diagram showing how the molecule's energy will be affected by *internal rotation*
    c. accurately assigning *dihedral (torsion) angles*, identifying *anti* and *gauche* isomers (bonds, groups), identifying *staggered* and *eclipsed* isomers (groups)
    d. accurately identifying sources of *torsional strain* and *van der Waals repulsion*

6. Predict the physical properties of alkanes, including relative *boiling temperatures*, relative *melting temperatures*, and *solubility* in water
   a. justify your prediction by appropriately invoking *van der Waals* and *molecular surface area*
7. Calculate a compound's "carbon footprint", i.e., the amount of carbon dioxide that would be released by complete combustion of the compound

Top 10 Problems for Chapter 2

Most of these problems are drawn from the *Additional Problems* located at the end of the chapter 2. Two problems, 21 and 22, are located inside the chapter.

The top 10 for chapter 2 are **21, 22, 27, 29, 30, 33, 36, 39, 45, 46**

Additional Readings

A ROCO reading that might prove helpful:

- *Molecular geometry* (provides additional information regarding *van der Waals radius*)

Supplement

Nomenclature

As you can see from the checklist, a substantial part of this chapter is devoted to "molecular anatomy", i.e., being able to recognize and name molecules and their parts. Unfortunately, students tend to react to the rules for naming compounds in the same way that sharks react to a bleeding surfer, but try to hold back. I can't emphasize the following too much:

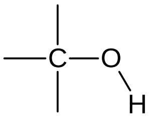
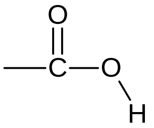
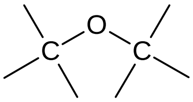
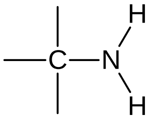
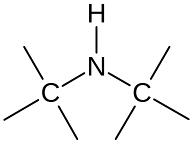
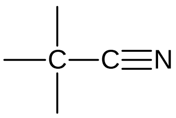
- A name is only a name. While you should learn to use technical names correctly, your ability to name things will ultimately prove to be a skill of relatively *minor* importance.
- I will not expect you to name things that I cannot easily and reliably name *myself* (and I am far from being an expert in these matters).
- Being able to name families (alkanes, alcohols, etc.), groups (*iso*-butyl, methylene, aryl, etc.), and structural units (*primary* carbon, *secondary* hydrogen, etc.) is often more important than being able to name specific molecules.

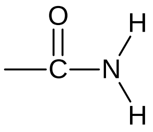
Tip – learn to *punctuate* chemical names correctly. There are simple rules for inserting commas and hyphens in chemical names:

- **hyphens** separate letters from numerals and numerals from letters (I list both combinations because it doesn't matter which item follows which). Thus, 3-methylpentane and 1-ethyl-2-methylcyclohexane.
- **commas** separate numerals. Thus, 3,3,4-trimethylhexane.

Functional groups

The checklist asks you to learn to recognize six functional groups. The following table shows the key atoms in these groups and what you should be looking for.

Names & formulas	Comments
Alcohol 	C is usually bonded to three other groups. C must *not* be double bonded to a 2^{nd} O since that would make this a carboxylic acid.
Carboxylic acid 	C must be bonded to *two* O; one double bond + one single bond. This structure is often written "-CO_2H" and "-COOH".
Ether 	O must be bonded to *two* C. Both C are usually bonded to three other groups. Neither C can be double bonded to a 2^{nd} O.
Amine  or 	N must be bonded to 3 atoms. Any combination of H and C is ok (only 2 of 4 possibilities are shown) but no C can be double bonded to O since that would make this an amide.
Nitrile 	C and N must be triply bonded. C is usually bonded to another C.

Amide 	C must be double bonded to O and single bonded to N. N must be bonded to 2 other atoms (the others need not be H as shown here).

Internal rotation

Rapid internal rotation is expected around all single bonds at room temperature. Loudon accurately points out the vast amount of thermal energy present at room temperature (p. 52), but here's another way to look at it: room temperature is almost 300 degrees higher in temperature (energy) than absolute zero. Boiling water, which feels hot to us and can easily burn our skin, is just another 75 degrees higher in temperature.

Since internal rotation occurs so easily (we often call it "free rotation"), a mixture of conformation isomers is always present and these isomers are at equilibrium, i.e., we can estimate the relative populations of these isomers by using the mathematical equations that connect energies, equilibrium constants, and concentrations.

Internal rotation is easily accomplished because it does not weaken the "rotating" bond. Consider the CC bonding molecular orbital in the staggered and eclipsed forms of ethane (Figure 2.3). In both cases, the bonding orbital is produced by combining two C *sp*^{3} orbitals and this overlap is equally effective regardless of the positions of the hydrogens.

Loudon states that the eclipsed form of any molecule is less stable because of *torsional strain* (p. 51). He describes the source of torsional strain as "repulsion … between the electrons in the [CH] bonds". That means torsional strain is caused by exactly the same "Pauli repulsion" that is used to explain bond angles in VSEPR. The only difference is that the "repelling" pairs of bonding electrons are connected to a single central atom when we talk about VSEPR, and to neighboring atoms when we talk about "torsional strain".