

## **SpartanModel Modeling Activity #1: Alcohol Structures & Properties**

### **Overview**

This activity describes the data collection steps for our experiment. Instructions for writing your lab report can be found in the online lab manual. Some of these instructions are paraphrased here so that the connection between data collection and the report is more obvious.

This activity also provides a small amount of background information about computer-based molecular models. This information is fairly minimal and interested students should come see me to learn more.

### **Background**


When you build a model using *SpartanModel*, two things happen, one visible, the other not. The visible part is the changing appearance of the molecule on your computer screen. The invisible part includes calculations that the computer is doing behind the scenes, as well as approximations that underlie these calculations. An example might help here.


Click **New** and build ethane,  $\text{CH}_3\text{CH}_3$  (simply connect two  $sp^3$  C atoms together). Measure the CC bond distance. You should obtain 1.531 Å. Now measure a CCH bond angle. You should obtain  $109.47^\circ$ . Where did these numbers come from?

The answer to this question goes straight to the heart of *SpartanModel's* "invisible" operations. Each time you added atoms to your molecule, *SpartanModel* was simultaneously 1) making a list of the atoms in the molecule, and 2) assigning Cartesian (x, y, z) coordinates to each atom. The coordinates were generated using a table of standard (typical) bond distances and angles, which is a plausible approximation. This explains why all of the bond angles are exactly  $109.47^\circ$ .

Unfortunately, actual bond distances and angles rarely correspond to "typical" values. If we want our models to represent actual molecules, we need a way of improving or refining the atom positions. Computational chemists call this refinement procedure "geometry optimization". Another term they use is "energy minimization" because the strategy for finding the optimal geometry is to move the atoms around until molecule's internal energy is as low as possible.

*SpartanModel* actually provides two tools for performing geometry optimization (energy minimization). One of

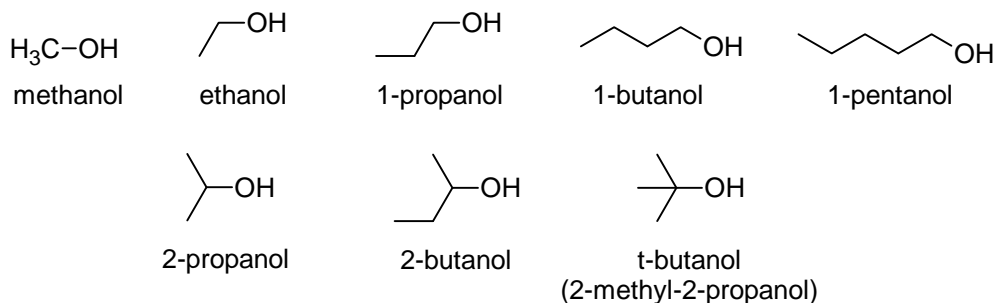
these is the **Minimize** button  (notice that it looks like an arrow pointing to "low E"). This tool uses a highly simplified method for calculating energy to produce "optimal" geometries in a hurry. These geometries

are not very reliable. The second tool is the **Properties** button  (the balloon seems to be saying "information here"). This tool relies on a much more sophisticated method for calculating energies. This method is not completely reliable either, and so you should know that there are many other tools available to computational chemists. Even so, the model geometries generated by the **Properties** button are usually quite informative.

Try clicking on the **Minimize** button. Measure and record a few bond angles. Have they changed? Have they changed much? Now click on the **Properties** button and re-measure these angles. Have they changed again? Have they changed much? Even though these three geometries, the model initially generated by building the molecule, the model generated by the **Minimize** button, and the model generated by the **Properties** button, are all fairly similar, we will generally regard the optimized geometries produced by the **Properties** button as the best that *SpartanModel* has to offer.

## Instructions

1. **Water.** Build a model of water. Optimize its geometry using the **Properties** button and check the Dipole Moment box. Next, display its potential map. You should be able to correlate the direction of the dipole moment arrow with the positions of extreme potential on the map. Click a few locations inside the red and dark blue regions of the potential map until you find what looks like the most extreme values of the electrostatic potential. Because we will be rounding off potentials to the closest  $\pm 5$  kJ/mol, it is not necessary to locate these points with perfect precision. Finally, compare the information you have gathered about water with the information in the table (see bottom of handout). Make your results agree with the information in the table and that you know how to obtain each item in the table.
2. **Alcohols.** One by one, build a model of each alcohol shown below and enter the relevant information in the table. (You should reproduce this table in your lab notebook on a right-hand page.) The following questions are intended to help you think about the questions you need to answer to write your lab report. You do not need to write the answers in the lab notebook, but you might want to make some notes here that you can refer to when you prepare your lab report.



## Questions

Chemists believe that “like dissolves like.” This is usually taken to mean that substances of similar (or “like”) *polarity* are mutually soluble. Here are three ways in which one might assess a molecule’s polarity:

- Dipole moment
- Range of electrostatic potential
- Percentage of surface area occupied by polar groups

The following questions ask you to examine these three properties across a series of molecules and see if you can find anything that might deepen your understanding of “like dissolves like”. They begin, however, with some questions that should help you better understand concepts like dipole moment, potential, and polar surface area.

1. *SpartanModel* calculates a molecule’s Area (total surface area) and Polar Surface Area using space-filling models and a strict definition of what counts as “polar surface”. In the case of your alcohols, an OH group is considered “polar surface” and “CH” groups are considered “nonpolar surface”. Take another look at the potential maps of your alcohols and the values of Area and Polar Surface Area that you recorded. What kinds of potentials are found near “polar surfaces” and “nonpolar surfaces,” respectively? Are they really that different?
2. *SpartanModel’s* potential map only shows potentials at a molecule’s “surface”. Atoms that are “buried” inside the surface don’t have much effect on displayed potentials, but they may still carry significant charges. Examine the potential map of methanol. Which bond looks more polar, the HO or CO bond? Now look at the dipole moment vector. Does its direction match that of the more polar bond? If it doesn’t, how would invoking two polar bonds help you explain its direction? (Note: the location of the vector relative to the molecule should be ignored. Just pay attention to the vector’s *direction*.) Do the dipole moment vectors of all of the alcohols point in similar directions?

3. The top line of alcohol formulas shows all of the "1-alcohols" that were studied in this experiment. (Note: You didn't make any measurements on 1-pentanol, but other chemists have established its solubility in water as 2.25% by weight.) Which alcohols are completely soluble? Which, if any, have low solubility? Is the dipole moment of these alcohols a good guide to solubility? How about the range of electrostatic potentials? How about the %polar surface area? Which property is a useful guide to the "like dissolves like" principle?
4. Three different C<sub>4</sub> alcohols were studied in this experiment. Identify them and note their relative solubilities. Within this group, does "like dissolves like" offer a good guide to alcohol solubility? (Note: In thinking about "like dissolves like", pay attention to the property(s) that you identified as useful in the previous question.)
5. Referring once again just to the C<sub>4</sub> alcohols, does an alcohol's boiling point correlate with its solubility in water? (Boiling point data should have been recorded in your lab notebook, but if it wasn't, find these data now.) According to the Background section for this experiment, under what conditions, enthalpy dominates mixing vs. entropy dominates mixing, is boiling point expected to correlate with solubility?
6. The solubilities of C<sub>5</sub> alcohols in water at 20°C have been measured (R. Stephenson *et al.*, *J. Chem. Eng. Data*, **1984**, 29, 287-290):
  - 1-pentanol 2.25% (bp 138°C)
  - 2-pentanol 4.64% (bp 118-119°C)
  - 3-pentanol 5.86%, (bp 116°C)
  - 2-methyl-1-butanol 2.83% (bp 129°C)
  - 3-methyl-1-butanol 2.64%, (bp 130°C)
  - 2-methyl-2-butanol 11.5% (bp 102°C)

Can you explain these data better using "like dissolves like" or some other principle?

Bottom-line: "Like dissolves like" is a nice rule-of-thumb and suffices in many situations, but solubility is a complicated phenomenon.

**Data Table** (complete; copy into your notebook on right-hand page)

<b>Molecule</b>	<b>Dipole Moment (debye)</b>	<b>Most Negative Potential (kJ/mol) <math>\pm 5</math></b>	<b>Most Positive Potential (kJ/mol)</b>	<b>Area (<math>\text{\AA}^2</math>)</b>	<b>Polar Surface Area (<math>\text{\AA}^2</math>)</b>	<b>%Polar Surface</b>
Water	2.4	-260	240	36.2	36.2	100%
Methanol						
Ethanol						
1-Propanol						
1-Butanol						
1-Pentanol						
2-Propanol						
2-Butanol						
<i>t</i> -Butanol						