Chemistry Internal Assessment

Positive inductive effect of methyl groups in nine simple alcohols

1. _The research question_

Bond length, bond strength and bond polarity are three variables that provide significant information about the reactivity of a bond. The position adopted by atoms when they bond, will result in a greater or smaller overlap of their orbitals and this can affect the energy needed to break the bond. The scenario is even more complicated in real molecules bigger than diatomics as each bond is affected by the surrounding atoms and bonds. This is further complicated when they include atoms of different electronegativities resulting in polar bonds but when the geometry of the molecule cancels different pulls on shared electrons remaining non- polar in character. As a result of this chemical surrounding the electron density between the bonded atoms may decrease or decrease modifying the reactivity of a given bond. The polarity of a bond is directly determined by the density of the electron cloud on the atoms involved in a bond.

In this investigation I will be considering the changes introduced in the electron cloud density of the C-O bond in alcohols in terms of the surrounding atoms/groups of atoms, focusing in particular on methyl groups and intermediate CH_2. I will compare straight chain simple alcohols of different lengths and branched simple alcohols.

My hypothesis

The C-O bond in alcohols is of polar character as oxygen is more electronegative than C (1). As a result of this the electron cloud's density should be higher on the O rather than the C bonded to it. This results in a high concentration of negative charges on the O and a lower concentration on the C which is equivalent to stating the latter becomes more positive. Certain groups of atoms may reduce this uneven distribution of charges by allowing their electron clouds to move towards the partially positive C atom in what is called "positive inductive effect". Methyl groups belong to this type of groups.

The positive inductive effect becomes largest when methyl groups are directly bonded to the C bonded to the O in the hydroxyl group (identified as C_1 as from now). The greater room that electrons have for moving, reduces the repulsion forces also leading to a more stable structure. As more CH_2 are added this effect is substantially reduced so that it becomes 0 in the third carbon (2). Thus, the positive inductive effect of the methyl groups should be large in methanol reducing the partial positive charge on C_1. This inductive effect simply implies that the electron cloud of the group will be closer to the C_1 which then becomes slightly more negative counteracting the effect of the more electronegative O. Based on these arguments , the positive partial charge should increase from methanol to ethanol and then reduce in propan-1-ol. The values for butan-1-ol,

pentan-1-ol and hexan-1-ol should be the same considering the CH_2 separating the methyl group from C_1.

From the same stance, I expect butan-2-ol (a secondary alcohol) to show a more marked positive inductive effect than butan-1-ol (a primary alcohol) and 1-methylpropan-2-ol (a tertiary alcohol) to show an even stronger positive inductive effect as there are two methyl groups bonded to the C bonded to the O in the hydroxyl group.

2. *The procedure*

For checking the validity of my hypothesis I used molecular modeling. This tool allows producing the actual Electrostatic potential versus Electron density maps and will provide the information I need. According to T. Gardner (7) the electrostatic potential (ESP) is "the energy of interaction of a point positive charge with the nuclei and electrons of a molecule. Negative ESPs are areas with high electron density while positive ESPs correspond to areas with low electron density. These maps show actual distribution of charges and enabling me to investigate the validity of my hypothesis. The benefit of this tool is that "it reduces the complexity of the system, allowing many more particles (atoms) to be considered during simulations" (3). This is a tool used in Computational Chemistry that allows many interesting applications including the production of virtual labs which allow a detailed analysis of structures. This can help us understand many crucial topics including the reactivity of molecules, the building up of intermolecular forces and characteristics of materials.

The software I have chosen is Argus (5) which is slightly outdated, but it is simple to use and is for free. The results I have obtained are based on using Zindo which is classified as a semi-empirical, Hartree-Fock self-consistent field method. While widely used it provides a more accurate description of structure and properties. Electron potentials and electron densities can be separately mapped but I have chosen to map them together. Colours towards red indicate negative ESPs while colours towards blue indicate positive ESPs.
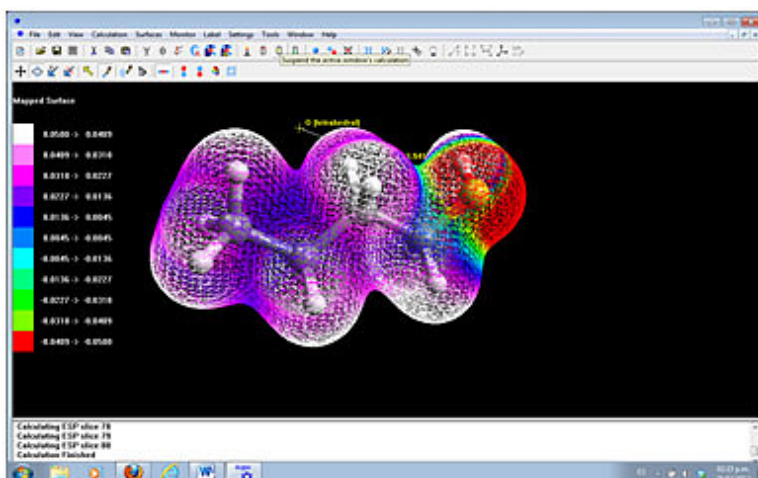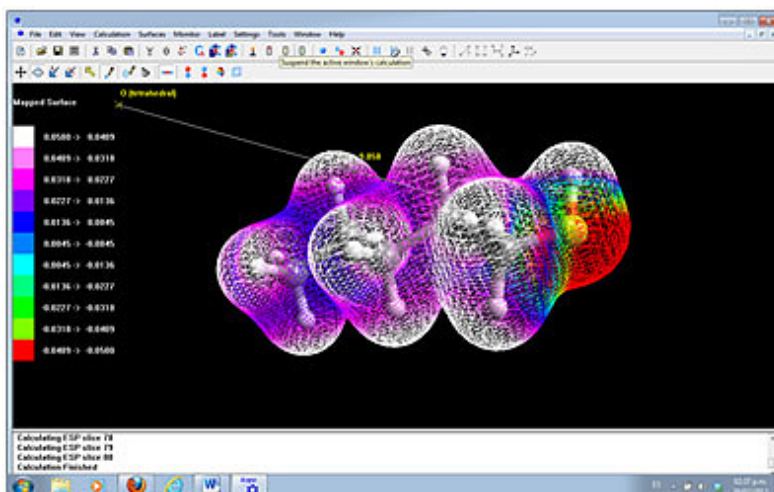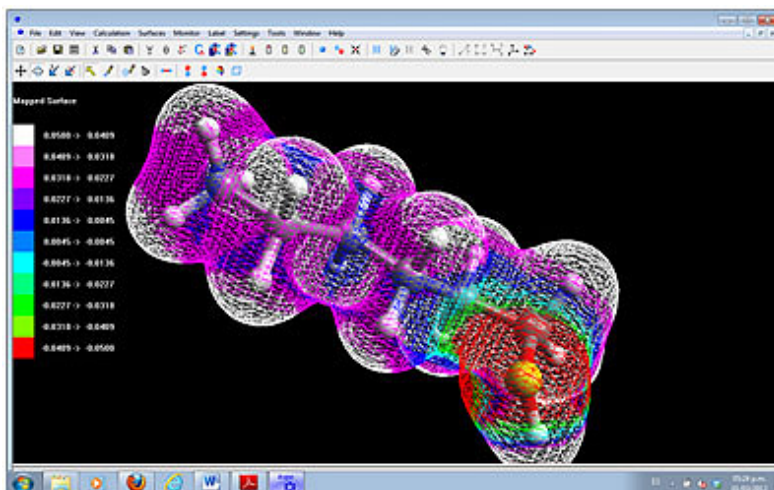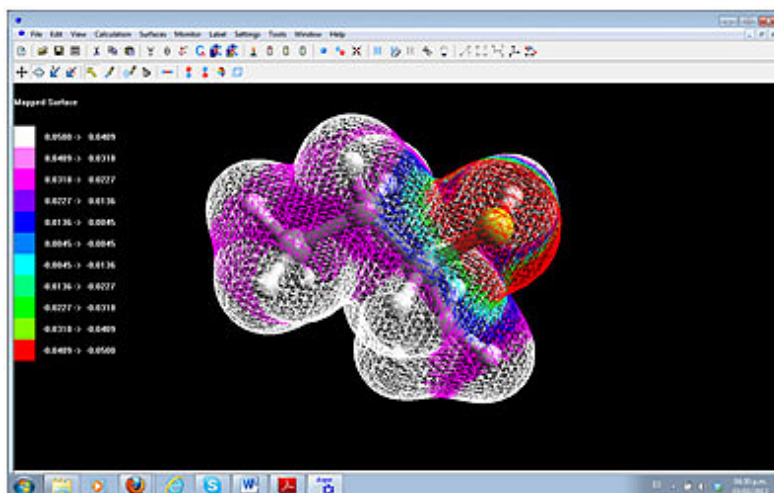
3. *Qualitative data*

Table 1. Colour codes in Hartree units

0.0500 ->	0.0409
0.0409 ->	0.0318
0.0318 ->	0.0227
0.0227 ->	0.0136
0.0136 ->	0.0045
0.0045 ->	-0.0045
-0.0045 ->	-0.0136
-0.0136 ->	-0.0227
-0.0227 ->	-0.0318
-0.0318 ->	-0.0409

The most positive potential value is represented by white with a value of 0.0500-0.0409 and the most negative by the red with the same range but negative in character. It is possible to convert from Hartrees to J mol^{-1} but calculations exceed my level.

Methanol
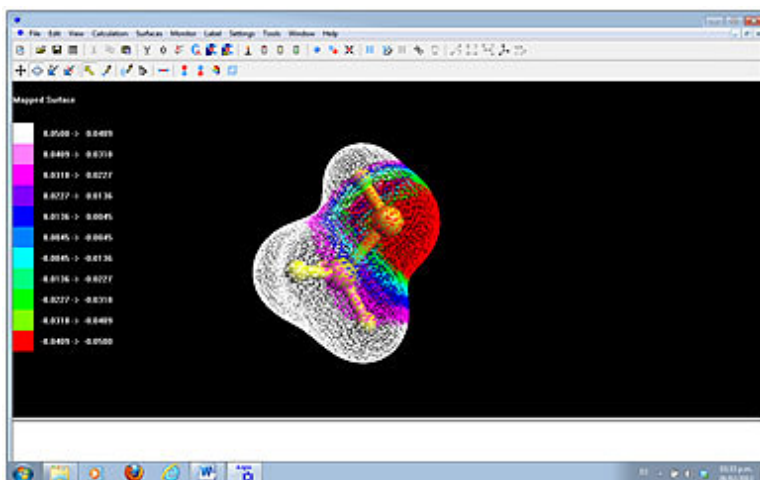
Ethanol:

Propan-1-ol

4
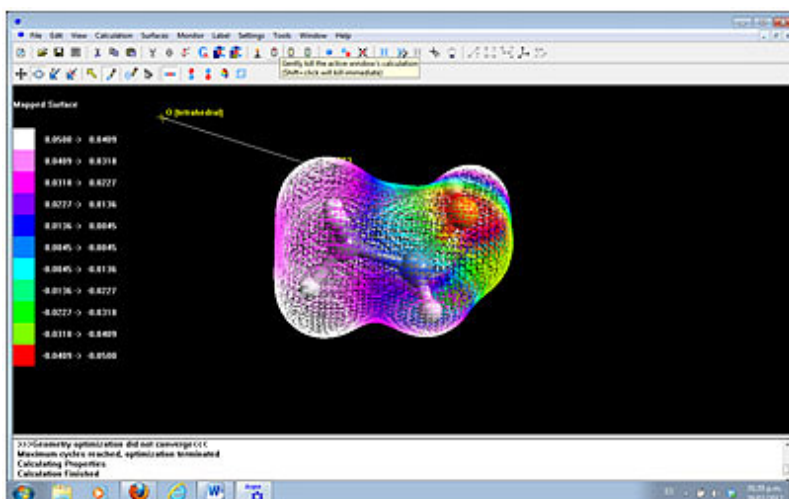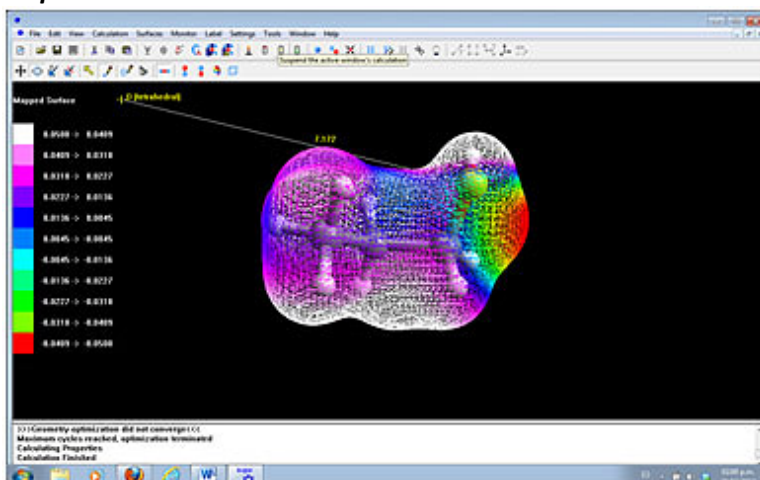
Butan-1-ol

Pentan-1-ol

Hexan-1-ol

5

Butan-2-ol

Propan-2-ol

2-methylpropan-2-ol

6
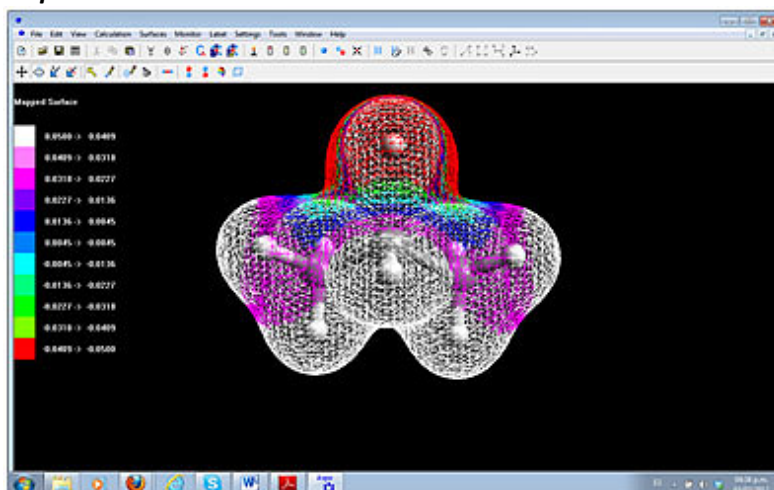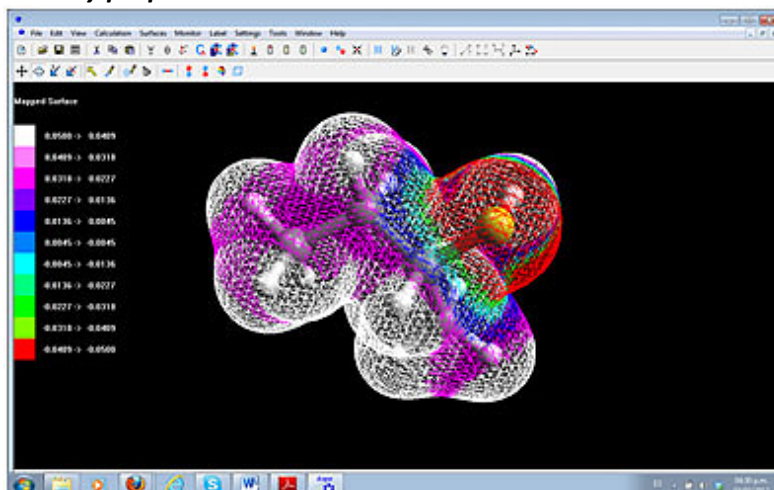
5. Analysis of qualitative data

The negative ESP is quite relevant in methanol which is consistent with my hypothesis that the methyl group would have a large positive inductive effect on C_1. It may be observed how the area surrounding the methyl group is mostly white (maximum positive potential) turning into red (maximum negative potential) on the O atom in the hydroxyl group. The cyan shows how negative potentials start in the bonding area close to the C. Therefore the electron cloud of the group has displaced towards the bond as it should otherwise appear entirely in pink or even white.

As a difference, in ethanol the pink areas (please refer to scale) start spreading towards the methyl group and so does the blue indicating that the electron cloud is more shifted towards the methyl group and therefore showing a reduced positive inductive effect.

In propan-1-ol the pink covers in a denser way the methyl group with a white area of substantially reduced relevance. The blue area spreads even further towards the methyl group. Thus, this shows an even more reduced positive inductive effect. This is as expected due to the intemediate CH_2.

The situation remains very much the same in butan-1-ol, pentan-1-ol and hexan-1-o which confirms that after the second CH_2 the positive inductive effect is zero.

In butan-2-ol where C_1 has one methyl group directly bonded it is positive to see again emerging white areas around the methyl group. This becomes even more marked in propan-2-ol where the number of methyl groups increases to two and in 2-methylpropan-2-ol where there are three.

 The distribution of the blue area is similar to that found in methanol even when in the first compound the methyl groups appear mostly in white. This is as expected because C_1 has two methyl groups bonded to it while in butan-2-ol there is only one. Consistent with expectations, the final methyl is more covered in pink in a way similar to the compounds mentioned above where it is separated by CH_2.

It is relevant to mention that is necessary to carefuly rotate the molecules to establish comparisons or else results may be misleading. I have found this a problem in presenting my data as it would otherwise involve a rather large number of images.

I am including one further image of the tertiary alcohol to illustrate this point. In it is quite clear how the area around the methyl groups is in white showing the displacement of the electron cloud towards the C_1.
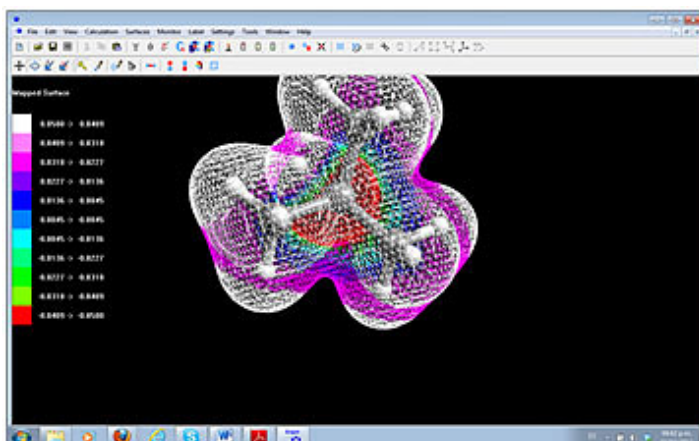
Another image resulting from rotating the molecule shows the red area focused on the O and the green area immediately surrounding the previous. Both colours stand for the most negative and second most negative ESPs.
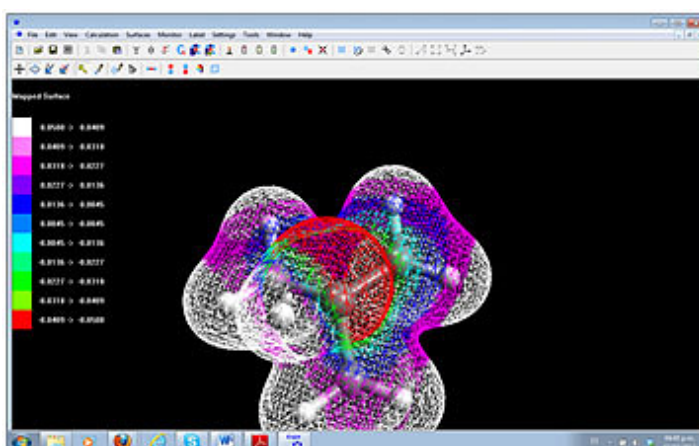
While doing this analysis I realized that maybe the electron density could clarify my previous observations.

For 2-methylpropan-2-ol the surface of the electron density is shown by the image below:

8
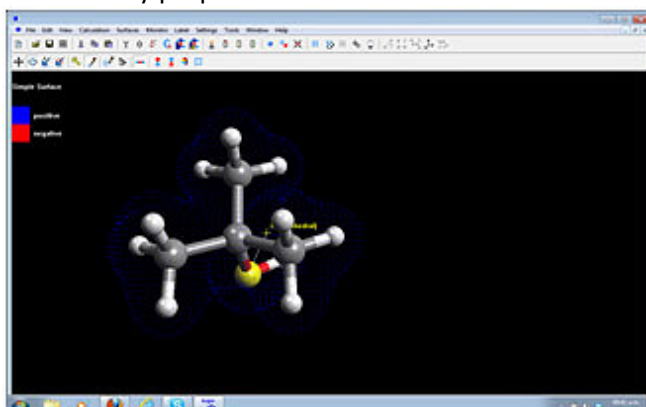
In this one the positive effect around the methyl groups is perhaps more evident and ratifies comments above.

6.Quantitative data

The previous analysis is based on purely qualitative data and this reduces its value. So in order to provide a more solid support to my analysis I will be using data provided by the Department of Chemistry of Colby College. Even when this database does not include all the structures considered in this investigation, those reported will provide some quantitative data which may support the previous analysis. One limitation imposed by this database is that calculations are done using Alain St-Amant's DeFT program (University of Ottawa) which is different to Argus. This could result in some discrepancies arising from the different calculation approach and I have no information on residual value for it. As any computational programme it is based on approximations.

Please observe that the author has numbered atoms in such a way that it is not possible to build tables for the sake of comparison. There is no information regarding uncertainties, thus the values entered are estimated in terms of number of significant digits reported

Table 2. Atomic Charges and Dipole Moment in methanol*

```
H3
   \
H5 - C1 - O2
   /      |
H4        H6
```

Atom	Charge ±0.001
C1	0.086
O2	-0.630
H3	0.088
H4	0.021
H5	0.020
H6	0.413
Dipole moment (±0.00001 Debye)	1.88296

*The site provides no units for charges so I have assumed they are based on the charge of an electron is considered   -1

Ethanol

```
    H5   H4
      \  |
H9      C3 - H6
 |     /
O1 - C2
     | \
   H8   H7
```

Atom	Charge ±0.001
O1	-0.677
C2	0.332
C3	-0.406
H4	0.104
H5	0.119
H6	0.093
H7	-0.027
H8	0.050
H9	0.411
Dipole moment (±0.00001 Debye)	1.88558

Table 3. Atomic Charges and Dipole Moment in ethanol

Propanol

```
H9  H10    O5 - H6
  \  |       |
     C3 - C4 - H12
   /          \
H1 - C2          H11
   | \
   H8   H7
```
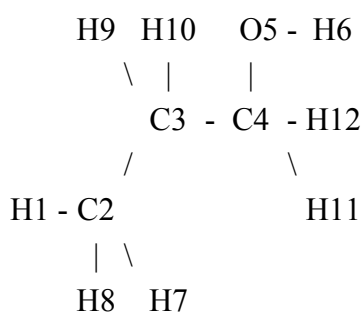
Table 4. Atomic Charges and Dipole Moment of propanol

Atom	Charge ±0.001
H1	0.138
C2	-0.546
C3	0.203
C4	0.149
O5	-0.692
H6	0.429
H7	0.130
H8	0.129
H9	0.014
H10	0.015
H11	0.013
H12	0.013
Dipole moment (±0.00001 Debye)	1.65032

Propan-2-ol

```
     H4    H5
       \   |
H12      C3 - H6
 |      /
 O1 - C2    H9
   | \ |
   H11  C7 - H8
        /
      H10
```
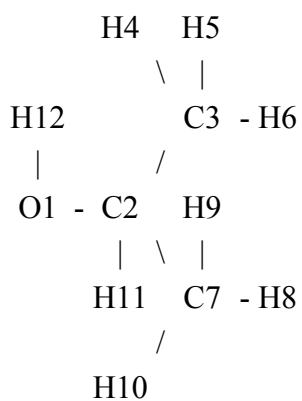
Atom	Charge ±0.001
O1	-0.698
C2	0.564
C3	-0.666
H4	0.167
H5	0.167
H6	0.166
C7	-0.679
H8	0.170
H9	0.170
H10	0.170
H11	0.053
H12	0.413
Dipole moment (±0.00001 Debye)	1.84941

2-methylpropan-2-ol

```
           H4
            \
 H15      H6  - C3  -
                    H5
  |            /
 O1   -   C2    H8
          |  \  |
3      -  C11  C7 -  H10
    /H14 /H12 / H9
```
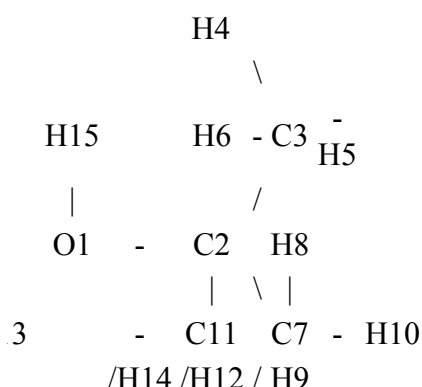
Atom	Charge ±0.001
O1	-0.709
C2	0.796
C3	-0.664
H4	0.148
H5	0.170
H6	0.162
C7	-0.668
H8	0.149
H9	0.163
H10	0.170
C11	-0.572
H12	0.161
H13	0.128
H14	0.162
H15	0.402
Dipole moment (±0.00001 Debye)	1.73513

Table 6. Atomic Charges and Dipole Moment in 2-methylpropan-2-ol

7. Comparison between qualitative and quantitative data

Table 7. Charge (±0.001) on C bonded with O

Methanol	Ethanol	Propanol	Propan-2-ol	2-methylpropan-2-ol
0.086	0.332	-0.546	0.564	0.796

I find these results rather baffling as the highest negative charge is on propanol where the inductive effect of the methyl group should be less marked because the methyl group is on the second carbon. I find the increase in charge between ethanol and methanol consistent as the C1 is not as affected by the inductive effect in the former. But then the charge becomes more positive in propan-2-ol where the C1 should receive the inductive effect of two methyl groups, and even more positive in 2-methylpropan-2-ol where the carbon bonded to the O is affected by three methyl groups. This contradicts the qualitative data and what I have learnt in the course.

I was further surprised to see that the different hydrogens in the methyl groups had different charges as well because the bonds involved are sigma and admit free rotation. Values were the same for one methyl group in propan-2-ol and very similar in the other methyl group of the same compound. Nevertheless, hydrogens in the latter were not showing exactly the same charge as I would have expected. I am also unable to explain the difference between both as this is a symmetrical molecule and to the best of my knowledge all the hydrogens should be equally

affected by the electronegative O. The estimated uncertainty does not cover the differences. Once again the quantitative results contradict the qualitative.

When comparing the charges on the Hydrogens, values become increasingly more positive in going from methanol to propanol and then increase even further in propan-2-ol. In terms of the 0.086 charge on the C in methanol, it is consistent that the charge on the hydrogens lowers as the electrons spread towards the C. In ethanol the charge on C increases positively which may be explained because the hydrogens are further away, but I fail to explain the increased positive charge on these hydrogens. Considering the inductive effect is reduced, this charge should be less positive. When going to propanol the charge on the hydrogens is even more positive and this could explain the negative charge on the C, but as the hydrogens are more distant the inductive effect should be smaller rather than larger.

In propan-2-ol the inductive effect does benefit the carbons adjacent to that bonded with O, but the latter shows a relatively high positive charge. In terms of what I have studied in the course it is the C bonded with the O the atom receiving the inductive effect and not its neighbours.

Table 8. Dipole moments of alcohols according to Schupf and NIST

Compound	Schupf (±0.00001 Debyes)	NIST (±0.01 Debyes)
Methanol	1.88296	1.70
Ethanol	1.88558	1.44
Propanol	1.65032	1.55
Propan-2-ol	1.84941	1.58
2-methylpropan-2-ol	1.73513	1.64

These values result on further doubts about the validity of Schupf's data. NIST is a highly reputed data base and the results are widely considered as reliable. Is not only that values differ significantly but the trends shown are also in conflict.

There is though a possibility that I have wrongly interpreted values corresponding to charges. Schupf's data show no units for them. I assumed these were based on arbitrary values as stated by several sources with -1 standing for the charge on an electron. When checking the NIST database I found that charges can be stated in several different types of units. This could explain the discrepancies but still offers no clarification for the contradictory dipole moments. I was unable to use the data from NIST as it requires a knowledge far exceeding my level.

6. Final reflections

I may finally conclude that my hypothesis was validated when using Argus and the qualitative data. These show an increasing positive inductive effect when methyl groups are directly bonded to the C bonded to the O and that this effect diminishes with intermediate CH_2, becoming negligible after the second CH_2.

My hypothesis is not supported by quantitative data which are also not consistent with what I have learnt in the course and found in references.

This investigation does present certain important limitations. I have not optimized the geometry as I am still not too familiar with Argus and I have used quantitative data using a different

programme to validate my qualitative data. It is very evident that this investigation should continue using qualitative and quantitative data resulting from the same programme.

I found of interest the comment found in a document at the site of Penn State Department of Chemistry (9) while looking for further programmes to compare data with those resulting from Argus:

'you should be critical and even skeptical of results produced by computational chemistry. One of the major limitations of all these computations is that they assume non-interacting molecules, in other words gaseous molecules in a vacuum. Obviously, reactions run in solvents involve solvent-molecule interactions that can significantly change the experimentally measured energetics from those predicted by calculation. (There are models that can estimate solvent effects.) It is quite possible to run a series of calculations that produce results that are absolutely meaningless. Therefore, it is imperative that you use your knowledge of organic chemistry and repeatedly ask, "Are these results consistent with what is observed experimentally and do they make sense using the traditional hand drawn arrow-pushing chemistry taught in textbooks?" If they don't, it probably means that you have chosen the wrong computational model to do the calculation'.

This would support my suggestion to look for another programme. Considering obtained results, Argus data are consistent with theory found in texts while those found in Schupf's database are not.

It is clear that results should be checked with experimental results and carefully analyzed. So for instance I would be interested in researching NMR values of these alcohols to find out if Schup's values are confirmed or rejected. I would also like to learn more about the differences in the units used for charges in computational analysis and their relative advantages. It would also be very interesting to obtain data with Spartan (11) which is a rather popular programme at college level.

7. References

(1) IB Data Booklet
(2) *web.uvic.ca/~chem213/213-5-11.ppt*   (Accessed February 2012)
(3) http://en.wikipedia.org/wiki/Molecular_modelling (Accessed March 2012)
(4) http://www.quantum-chemistry-history.com/Parr1.htm (Accessed March 2012)
(5) http://www.arguslab.com/arguslab.com/Welcome.html   (Accessed February 2012)
(6) Molecular modeling for beginners, A Hinchcliff (2003), Wiley
(7) http://www.wavefun.com/ (Accessed March 2012)
(8) Schupf PJ , Molecular Structure Calculations, http://www.colby.edu/chemistry/webmo/mointro.html (Accessed August 2012)
(9) Molecular Modeling, http://courses.chem.psu.edu/chem36/Chem36H/36H%20Web%20S'05/MolModThoery.pdf (Accessed August 2012)
(10) Experimental values of Electric dipole moment, http://cccbdb.nist.gov/ (Accessed August 2012)
(11) Hehre W, Shusterman A (2000),Molecular Modeling in Undergraduate Chemistry Education, Wavefunction Inc.