Chem 343–Spring 2007
Problem Set 1

1. In the boxes provided, give the **preferred hybridization** (that is \(sp^3\), \(sp^2\), \(sp\)) of indicated atoms (‘preferred hybridization’ refers to the hybridization in major contributing resonance form or in the resonance hybrid).

   (a) \(\text{SP}\)  
   (b) \(\text{SP}^2\)  
   (c) \(\text{SP}^2\)  
   (d) \(\text{SP}^2\) considering another resonance form  
   (e) \(\text{SP}^2\) considering two additional resonance forms  
   (f) \(\text{SP}^2\)

2. In the boxes provided, describe the indicated bonds in terms of their component molecular orbitals (appropriate resonance forms should be considered).

   (a) Example  
   (b) \(\sigma_{\text{C}_{\text{sp}^2}\text{O}_{\text{sp}^2}}\)  
   (c) \(\sigma_{\text{B}_{\text{sp}^2}\text{C}_{\text{sp}^3}}\)  
   (d) \(\sigma_{\text{C}_{\text{sp}}\text{C}_{\text{sp}^2}}\)  
   (e) \(\sigma_{\text{B}_{\text{sp}^3}\text{O}_{\text{sp}^3}}\)  
   (f) \(\sigma_{\text{C}_{\text{sp}^2}\text{N}_{\text{sp}^2}}\)

3. Circle the more polar compounds in each pair.

   (a) \(\text{Cl-Cl}\) vs \(\text{Cl-Cl}\)  
   (b) \(\text{CHCl}_3\) vs \(\text{CCl}_4\)  
   (c) \(\text{CH}_3\) vs \(\text{O}\)  
   (d) \(\text{SO}_2\) vs \(\text{CO}_2\)

4. (a) Draw the best **Lewis structure** for the following compounds. Put in all lone pairs and multiple bonds and formal charges.
(b) Write two additional resonance structures for acetylacetonate anion. Put in all lone pairs and multiple bonds and formal charges. How well does each describe the structure of the compound? Using these resonance structures describe the real charge distribution in the anion (What is the approximate charge on each oxygen and on the central carbon? For each oxygen: -0.5, between -0.5 and -0.33, -0.33, less than -0.33. For the center carbon: -0.5, between -0.5 and -0.33, -0.33, less than -0.33.)

(c) Acetylacetone $\text{CH}_3\text{COCH}_2\text{COCH}_3$ ($\text{pK}_a = 9$) is much more acidic than acetone $\text{CH}_3\text{COCH}_3$ ($\text{pK}_a = 19$). Explain in terms of resonance stabilization of the four species (acetone, acetone anion, acetylacetone, and acetylacetonate anion) needed in the comparison.

5. **Coumadin** is an anticoagulent that was discovered at the University of Wisconsin by Karl Paul Link in 1956. It was patented by the Wisconsin Alumni Research Foundation and is also known as Warfarin. It's structure is drawn below.
(a) What is the molecular formula of Coumadin?
\[ \text{C}_{19}\text{H}_{15}\text{O}_{4}\text{Na} \]

(b) Rewrite the structure of coumadin putting in all hydrogen atoms, lone pairs of electrons, and formal charges.

(c) Write a second Lewis structure of another resonance structure for coumadin, which has formal charge on a different atom.

(d) Estimate the relative energies of the two resonance structures. Is one substantially more stable (lower in energy)? If so, why? Or, are the energies of the two resonance structures nearly the same?

The two resonances are similar in their energies—octets at all atoms, negative charge on more negative oxygen atoms and etc.

(e) Use this information to discuss the negative charge distribution in coumadin and the relative lengths of the C–C bonds and C–O bonds in the oxygen containing six member ring of coumadin.

The negative charge is approximately equally distributed on the two oxygen atoms as shown in two resonance structures above. There would be a small negative charge distribution on the carbon (carbon 3) midway between the two oxygens. C(2)–C(3) and C(3)–C(4) bonds would be similar in their length and intermediate between a single and a double bond. O(1)–C(2) and O(5)–C(4) bonds would be similar in length and intermediate between a single and a double bond.

6. The following molecule is called Calyculin A.
   a. Draw a box around the alcohol functional groups on the carbon backbone of this molecule. How many are there? <5>
   b. Circle the amide functional groups. How many are there? <1>
   c. Draw an arrow towards the nitrile functional groups? How many are there? <1>
What is the hybridization of the carbon from which the nitrile group is attached? \(<sp^2>\)

d. Draw triangle around an amino functional groups. What type of amine is this? tertiary amine (3°)

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7. (a) Trimethylamine N(CH₃)₃ is a pyramidal molecule. Draw a Lewis structure of trimethylamine (put in all lone pairs and multiple bonds and formal charges). What is the hybridization at nitrogen?

(b) In contrast, formamide HCONH₂ has a planar nitrogen center. What is the hybridization at nitrogen? Draw the most important contributing resonance structures for formamide (put in all lone pairs and multiple bonds and formal charges). Explain why the hybridization at nitrogen is different for trimethylamine and formamide.

(c) Compound A shown below is often described as a vinylogous amide. That is, it's structure (planar at nitrogen) and reactivity (slow addition of hydroxide to the carbonyl carbon) are similar to that of formamide. Use resonance structures (put in all lone pairs and multiple bonds and formal charges) to explain the similarity of A and formamide.
The two most important resonance structures for these two compounds are very closely related. The minor contributors have octets at all atoms and negative charge at the electronegative oxygen.

8. An experimental technique called $^{13}$C Nuclear Magnetic Resonance Spectroscopy (you don’t have to know what it is to solve this problem) allows chemists to tell how many different kinds of carbons there are in a molecule and whether carbons are primary (1°), secondary (2°), tertiary (3°), or quaternary (4°). Give Kekule structures (i.e., use lines for electron pair bonds) for the following compounds having molecular formula C$_6$H$_{12}$. Also, on each structure, identify carbons as 1°, 2°, 3°, or 4°; tell how many different kinds of C’s there are; and designate which C’s are equivalent.

(a) A compound having only single bonds and only secondary carbons.

(all 2° carbons
all equivalent
one kind of carbon)

(b) A compound having only single bonds and primary, secondary, and tertiary carbons.

(4 different carbons
1°, 2°, 3° carbonds
two different 2° carbons)

(c) A compound having only single bonds and only primary, secondary, and quaternary carbons.

(4 different carbons
4°
1°)

5
(d) A compound having only single bonds and primary, secondary, tertiary, and quaternary carbons.

three 1° carbons - all different
one 2° carbon
one 3° carbon
one 4° carbon

9. There are many isomers with the formula C₇H₁₀O₂. How many (\(\pi\)-bonds + rings) do all of these isomers have? Draw specific examples that incorporate the following restrictions:

(a) An ester with a quaternary carbon.

(b) A compound with both an alcohol and an ether functional group.

(c) An alkyne

(d) An unsaturated carboxylic acid.

10. Indicate the direction of dipole moment on each compound and circle around the molecule has the largest dipole moment.
11. a) Circle one of the two strongest Lewis Acids shown below. Draw a Box around one of the two strongest Lewis Bases shown below.

\[
\text{N(CH}_3\text{)}_3 \quad (\text{CH}_3\text{)}_3\text{C}^- \quad (\text{CH}_3\text{)}_3\text{CH} \quad (\text{CH}_3\text{)}_3\text{C}^+ \quad \text{B(}\text{CH}_3\text{)}_3 \quad \text{H}_2\text{C=CH}_2
\]

**See four different combinations.

\[
\begin{align*}
\text{N(CH}_3\text{)}_3 & \quad (\text{CH}_3\text{)}_3\text{C}^- \quad (\text{CH}_3\text{)}_3\text{CH} \quad (\text{CH}_3\text{)}_3\text{C}^+ & \quad \text{B(}\text{CH}_3\text{)}_3 & \quad \text{H}_2\text{C=CH}_2 \\
\text{N(CH}_3\text{)}_3 & \quad (\text{CH}_3\text{)}_3\text{C}^- \quad (\text{CH}_3\text{)}_3\text{CH} & \quad (\text{CH}_3\text{)}_3\text{C}^+ & \quad \text{B(}\text{CH}_3\text{)}_3 & \quad \text{H}_2\text{C=CH}_2 \\
\text{N(CH}_3\text{)}_3 & \quad (\text{CH}_3\text{)}_3\text{C}^- & \quad (\text{CH}_3\text{)}_3\text{CH} & \quad (\text{CH}_3\text{)}_3\text{C}^+ & \quad \text{B(}\text{CH}_3\text{)}_3 & \quad \text{H}_2\text{C=CH}_2 \\
\text{N(CH}_3\text{)}_3 & \quad (\text{CH}_3\text{)}_3\text{C}^- & \quad (\text{CH}_3\text{)}_3\text{CH} & \quad (\text{CH}_3\text{)}_3\text{C}^+ & \quad \text{B(}\text{CH}_3\text{)}_3 & \quad \text{H}_2\text{C=CH}_2
\end{align*}
\]

(b) Draw the structure of the Lewis Acid-Lewis Base complex formed by reaction of the two species you indicated above. Show all lone electron pairs and formal charges.

**One of four complexes you can come up with from the above combinations

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H}_3 \quad \text{H}_3\text{C} \quad \text{C} \quad \text{B} \quad \text{C} \quad \text{H}_3 \quad \text{H}_3\text{C} \quad \text{N} \quad \text{C} \quad \text{C} \quad \text{H}_3
\end{align*}
\]

12. Determine the relative acidity of acetic acid and ethanol. Give an explanation that can support your decision based on inductive effect and resonance effect.

more acidic

\[
\begin{align*}
\text{acetic acid} & \quad \text{H}_2\text{C=O} \quad >> \quad \text{ethanol} & \quad \text{O} \quad \text{H}
\end{align*}
\]
1. Inductive effect-based rationale

First view: The strongly electronegative oxygen atom is directly attached to the carbon bearing O–H group in acetic acid but only non-electronegative two hydrogens are attached to the same carbon in ethanol, which makes the acetic acid more acidic than ethanol.

Second view: In acetic acid, an electron-withdrawing acetyl group (CH₃CO-) is attached to O–H group while an electron-releasing ethyl group is attached to the O–H group in ethanol, thus an acetic acid becomes more acidic than ethanol.

2. Resonance effect-based rationale

Once the acetate anion is generated, the two identical resonance structures can delocalize the anion efficiently over the two oxygen atoms. But the anion (ethoxide) generated from the ethanol does not have such electron delocalization mechanism because there is no π-bond in the system.

Also, in acetic acid, there isn’t much resonance stabilization but once the acetate anion forms, greater resonance stabilization is possible, which make the ionization less unfavorable. (For more details, see page 117 in the textbook)

13. Write a mechanism for the conversion of tert-butyl alcohol to tert-butyl chloride with concentrated aqueous HCl.
14. **Circle** the strongest acid and briefly explain why it behaves that way.

\[ \text{H}_2\text{S} \quad \text{HF} \quad \text{H}_2\text{O} \quad \text{HBr} \]

***HBr is strongest acids because the conjugate base \( \text{Br}^- \) is most stable compared to \( \text{HS}^-, \text{F}^-, \text{HO}^- \) because of the electron delocalization in large volume.***

15. **Number** the following in order of **increasing basicity** (a, b) and **increasing acidity** (c, d).

(a) \( \text{CH}_3\text{NH}_2, \text{CH}_3\text{NH}_3^+, \text{CH}_3\text{NH}^- \)

\[
\begin{array}{ccc}
2 & 1 & 3
\end{array}
\]

(b) \( \text{H}_3\text{C}\text{C}==\text{CH}^-, \text{CH}_3\text{CH}_2\text{CH}_2^-, \text{H}_3\text{C}\text{C}==\text{C}^- \)

\[
\begin{array}{ccc}
2 & 3 & 1
\end{array}
\]

(c) \( \text{H-Br}, \quad \text{H-F}, \quad \text{H-I}, \quad \text{H-Cl} \)

\[
\begin{array}{ccc}
3 & 1 & 4 & 2
\end{array}
\]

(d) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}, \quad \text{CH}_3\text{CH}_2\text{CO}_2\text{H}, \quad \text{CH}_3\text{CHClCO}_2\text{H} \)

\[
\begin{array}{ccc}
1 & 2 & 3
\end{array}
\]

16. Draw Newman projections of 1-chloro-3,3-dimethylbutane looking down the C(1)-C(2) bond to show,

(a) a **gauche** relationship between the chloro and tert-butyl groups

(b) an **anti** relationship between the chloro and tert-butyl groups
(c) the eclipsed conformation which is the transition state between the two gauche conformations

(d) Draw Newman projections of the three different staggered conformers of 2-chlorobutane looking down the C(2)-C(3) bond. Which group is sterically larger, chloro or methyl? Which of these staggered conformations is the most stable? Which is the least stable?

**Methyl group is larger than chloride group

17. Draw the structure of the following compounds. Use perspective drawings (i.e. for cyclohexanes show the conformation clearly.)

(a) A dimethylcyclohexane with two identical chair conformations.

(b) A compound in which the most stable conformation has two axial methyl groups on the same face of a cyclohexane ring.
(c) A compound in which the **most stable conformation** has **two axial methyl groups** on the **opposite faces** of a cyclohexane ring.

![Diagram of a compound with two axial methyl groups](image)

(d) A dichlorocyclohexane having **no net** molecular **dipole moment**.

![Diagram of a dichlorocyclohexane](image)

18. (a) Draw the most stable conformation of the **most stable** isomer of 1-bromo-3-methylcyclohexane. Is this a cis or trans isomer? For each substituent, indicate whether it occupies an axial or equatorial site.

![Diagram of the cis-isomer of 1-bromo-3-methylcyclohexane](image)

(b) Draw the most stable conformation of the **most stable** isomer of 1-bromo-4-methylcyclohexane. Is this a cis or trans isomer? For each substituent, indicate whether it occupies an axial or equatorial site.

![Diagram of the trans-isomer of 1-bromo-4-methylcyclohexane](image)

(c) Draw the **most stable** conformations of the other isomers (cis/trans) of 1-bromo-3-methylcyclohexane and 1-bromo-4-methylcyclohexane. Label the compounds as cis or trans isomers. For each substituent, indicate whether it occupies an axial or equatorial site.
19. (a) Draw the most stable conformations of cis- and trans-1,3-dimethylcyclohexane. Indicate the methyl groups as “axial” and “equatorial” on each conformer.

(b) Draw the most stable conformations of cis- and trans-1,2-dimethylcyclohexane and indicate which is more stable compound.

(c) What is the energy difference between the two isomers? Use 3.8 kJ/mol for a gauche interaction (In order to get full credit, you must describe how you reached your conclusion).

***Between the two structures above, there are net two gauche interaction difference, thus, in terms of energy difference it will be 2x3.8 kJ/mol (or 0.9 kcal/mol) = 7.6 kJ/mol (1.8 kcal/mol).

(d) Estimate the ratio of the more stable conformer to the less stable conformer of methylcyclohexane at 25 °C. (You may use \( \Delta G^\circ = -2.303RT\log K_{eq} \), \( R = 8.314 \times 10^{-3} \) kJ/mol°K, °K = °C + 273.16)
two gauche interaction difference

\[ \Delta G^\circ = -7.6 \text{ kJ/mol} \]

By using an equation, \( \Delta G^\circ = -2.303RT \log K_{eq} \)

\[
\log K_{eq} = \frac{-7.6 \text{ kJ/mol}}{2.303(8.314 \times 10^{-3} \text{ kJ/mol}^\circ \text{K})(273+25)^\circ \text{K}} = 1.33
\]

\[ K_{eq} = 10^{1.33} = 21 \]

\[
K_{eq} = \frac{\text{Equatorial-Me conformer}}{\text{Axial-Me conformer}} = 21 = \frac{21}{1}
\]

In total 22 parts of molecule, 21 parts are equatorial-Me conformers and 1 part is an axial-Me conformer.

Thus, the percentage ratio will be 95:5 from a simple calculation.

Equatorial-Me conformer: \( \frac{21}{22} \times 100 = 95\% \)

Axial-Me conformer: \( \frac{1}{22} \times 100 = 5\% \)