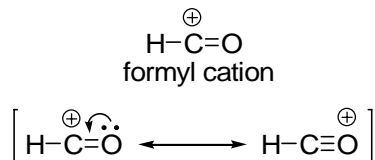


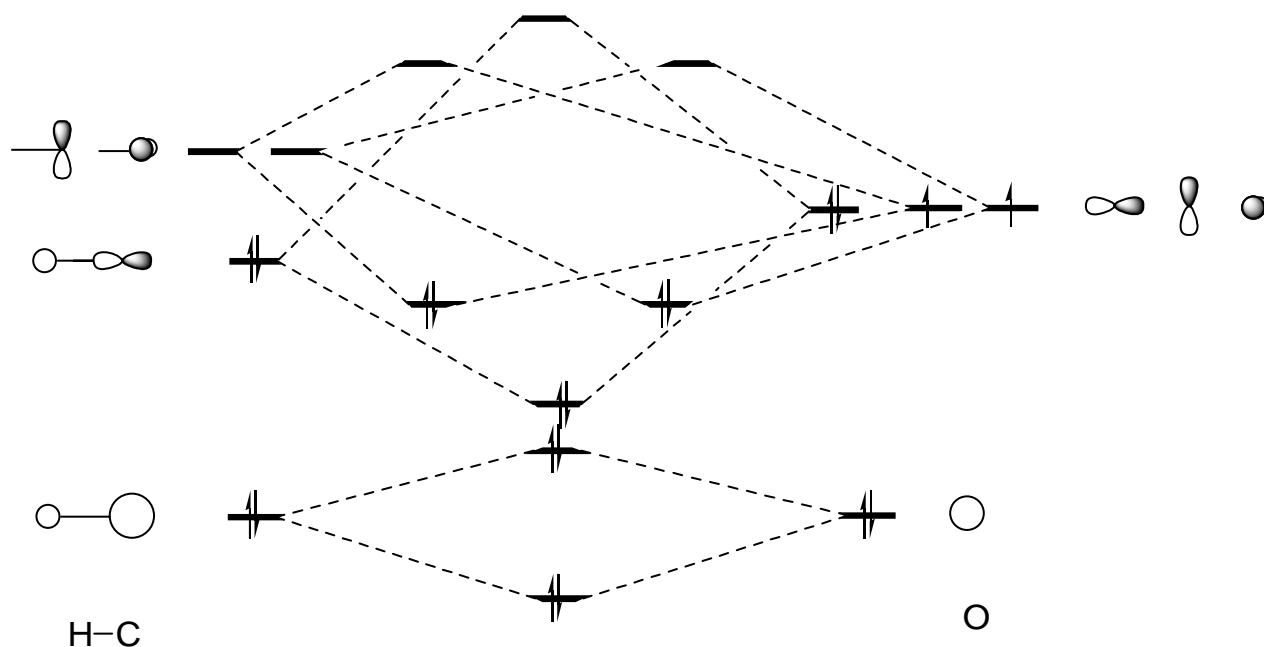
**CHEMISTRY 412/512**  
 MIDTERM # 1 – answer key  
 February 14, 2007

1. (8 pts) Acyl cations ( $R-\overset{\oplus}{C}=O$ ) are key intermediates in *Friedel – Crafts* acylation reactions. They are stabilized by the presence of oxygen and this can be demonstrated through either resonance or MO analysis.
- a. Consider the formyl cation, shown below. Show how it is stabilized, using appropriate resonance structures.



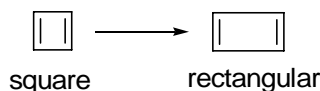
Acyl cations are stabilized by conjugation of one of the lone pairs at the oxygen center.

- b. Construct the orbital mixing diagram for the formyl cation, starting with group orbitals for CH and O-atom. Consider only first order mixing. Place the appropriate number of valence electrons and demonstrate how QMOT explains the stabilization of the cation.

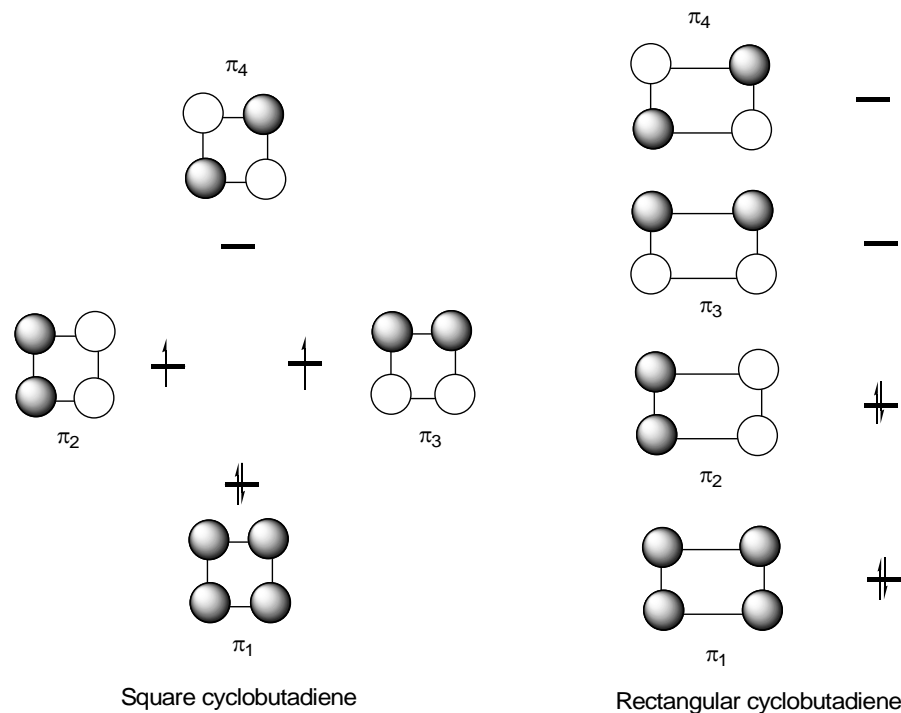


The mixing diagram clearly shows the formation of TWO equivalent  $\pi$ -bonds, which is analogous to the resonance structure on the right, i.e. there is significant contribution by the O-atom.

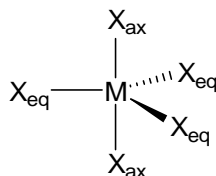
2. (6 pts) Antiaromatic molecules avoid antiaromaticity by structural distortion. For example, cyclobutadiene is not square (and antiaromatic) but rectangular. Show, using  $\pi$ -group orbital analysis, that such distortion would indeed be stabilizing.



**Solution:** Instability of square cyclobutadiene is due to the presence of two degenerate, half-filled  $\pi$ -molecular orbitals ( $\pi_2$  and  $\pi_3$ ). In the rectangular form, qualitatively, the MOs remain the same, but the strength of some bonding/antibonding interactions is affected and it causes the degeneracy to be lifted. Focus on  $\pi_2$  and  $\pi_3$ . Upon stretching, the antibonding interaction in  $\pi_2$  is reduced, while the same geometric distortion leads to reduction of the bonding interaction in  $\pi_3$ . As a consequence,  $\pi_2$  becomes lower in energy than  $\pi_3$  and we end up with two completely filled MOs:  $\pi_1$  and  $\pi_2$ . The resultant species is more stable.

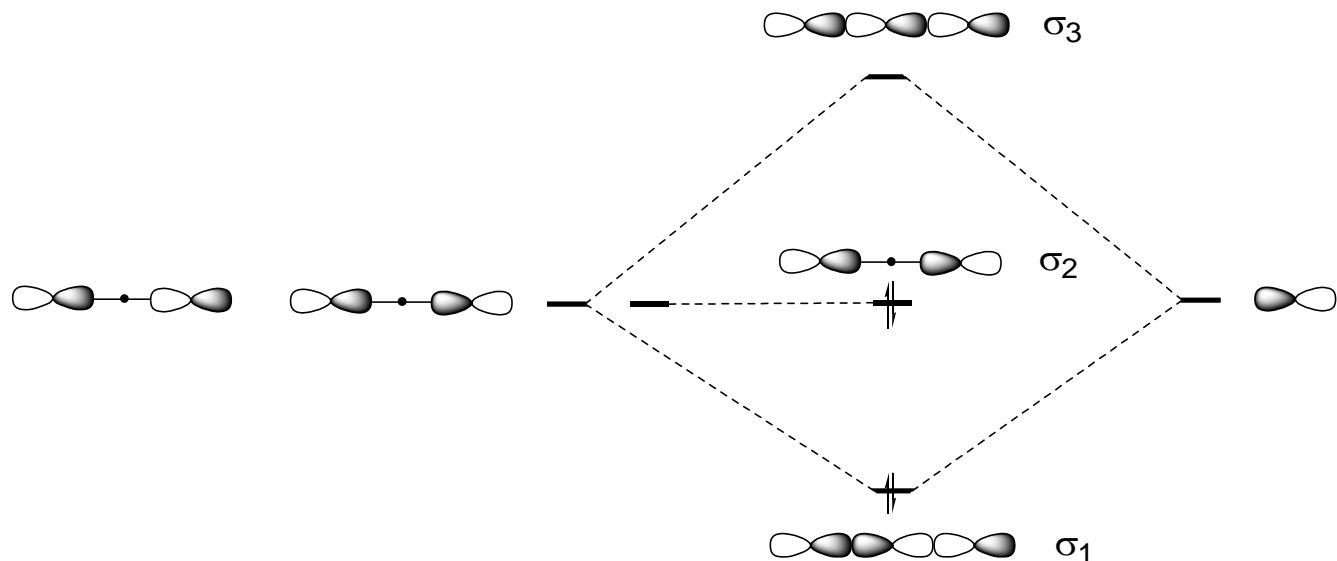


3. (6 pts) **This problem treats 3-center-4-electron bonds:** Species with formula  $\text{MX}_5$  exist in trigonal bipyramidal geometry, as shown below. To explain bonding in such molecules, especially in introductory courses, participation of  $d$ -orbitals is invoked. A number of studies have shown, however, that for main group elements (such as C, P, S, Cl, etc.)  $d$ -orbitals are much higher in energy compared to  $s$ - and  $p$ -orbitals, and cannot effectively mix with them, in order to form  $sp^3d$  hybrid orbitals and the necessary number of bonds. A more comprehensive view is based on the 3-center-4-electron bond. The central atom is envisioned in  $sp^2$ -hybridization state, using the  $sp^2$ -hybrid orbitals to form the three equatorial bonds to  $\text{X}_{\text{eq}}$ . Bonding to the axial groups is realized by the use of the single, unhybridized  $p$ -orbital of M, which combines with appropriately oriented  $p$ -orbitals of the  $\text{X}_{\text{ax}}$  groups, to form what is actually a 3-center-4-electron bond.

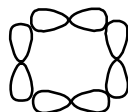


- Consider the fragment  $\text{X}_{\text{ax}} - \text{M} - \text{X}_{\text{ax}}$ . Use a  $p$ -orbital at each of the centers to construct the mixing diagram for the 3-center-4-electron bond.
- Consider the particular case of  $\text{CX}_5^-$ . It is a good approximation to the transition state for  $S_N2$  reactions. Fill the mixing diagram with the appropriate number of electrons.
- It is well known that in trigonal bipyramids the most electronegative substituents always tend to be axial. Account for it based on your mixing diagram analysis.

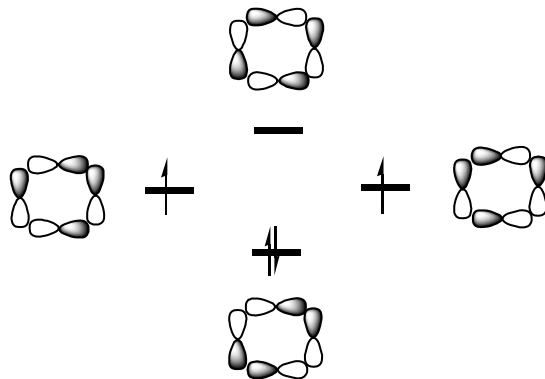
**Solution:** You can use the approach that we utilized for the allylic system. Construct a bonding and antibonding combination from the two terminal orbitals, then mix with the  $p$ -orbital of the central atom. Only one of the two terminal orbital combinations (the antibonding one) can mix. The result is a total of three MOs, of which the middle one has contributions only from the terminal atoms. It is the HOMO for a 3-center-4-electron bond. The conclusion then would be that the two terminal centers  $\text{X}_{\text{ax}}$  would receive this entire pair of electrons that resides in the HOMO. The more electronegative they are the better. Hence electronegative groups generally tend to reside on axial positions.



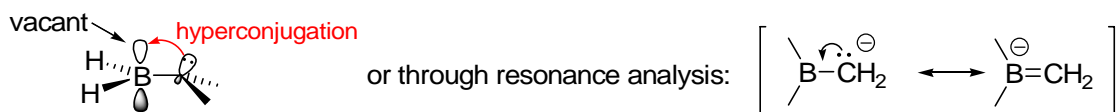
4. (6 pts) **This problem is about  $\sigma$ -aromaticity:** We are inclined, almost instinctively, to associate aromaticity with cyclic conjugated  $\pi$ -systems. The fact of the matter is, however, that aromaticity is a broader phenomenon that can occur in any type of system, as long as we have a cyclic array of orbitals. If they overlap in a  $\sigma$ -bonding fashion, then this could give rise to a  $\sigma$ -aromatic or antiaromatic system. Consider the cyclic array of four  $p$ -orbitals, shown below. Construct the group orbitals for this system and fill in the appropriate number of electrons (starting with one electron per  $p$ -orbital). Show that the resultant system is  $\sigma$ -antiaromatic.



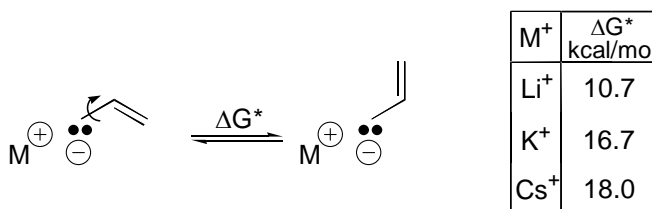
**Solution:** Since we have four  $p$ -orbitals as input, we should come up with four  $\sigma$ -molecular orbitals. One could use the approach that we applied previously to  $\pi$ -systems, namely start with a fragment consisting of two orbitals, combined in a bonding and antibonding fashion, then combine two such fragments, again in a bonding and antibonding fashion, limiting oneself only to first order mixing. The result is shown below. Of the resultant four  $\sigma$ -orbitals, only the first ( $\sigma_1$ ) is fully occupied. The degenerate pair ( $\sigma_2$  and  $\sigma_3$ ) have one electron each. Hence we predict that the resultant system will be unstable,  $\sigma$ -antiaromatic.



5. (8 pts) The following questions deal with stability and structure of particular carbanions. Offer a structural rationalization for each one.
- According to calculations the  $\text{BH}_2$  group is almost as stabilizing to carbanions as a  $\text{CN}$  or a  $\text{CF}_3$  group, even though boron is less electronegative than carbon.

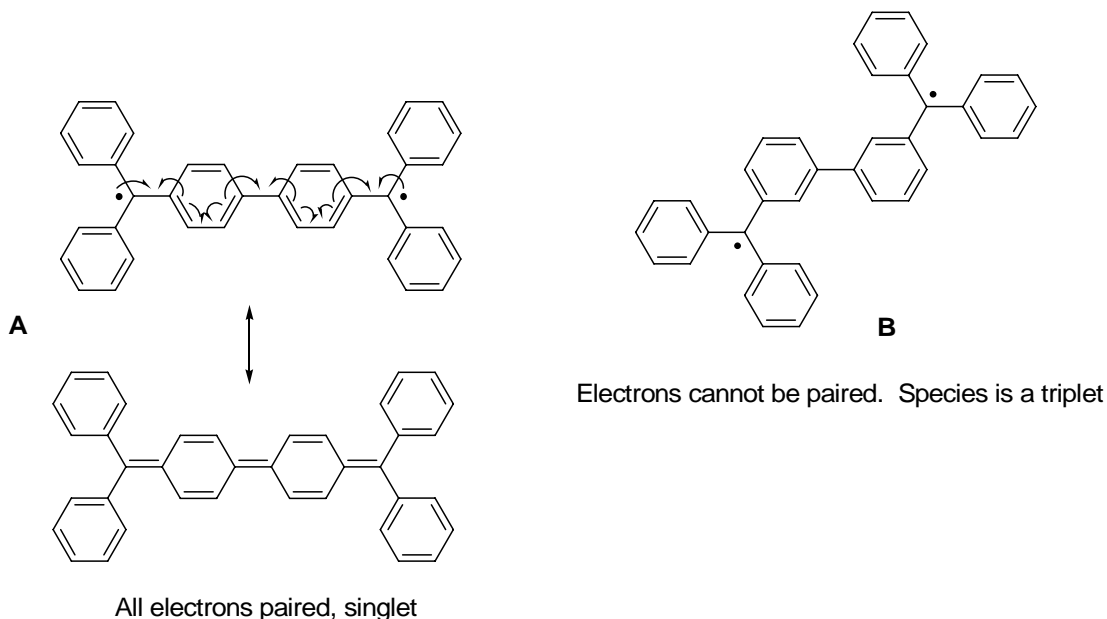


b. The rotational barrier in the allyl anion shows an obvious dependence on the counter ion (See results below!).

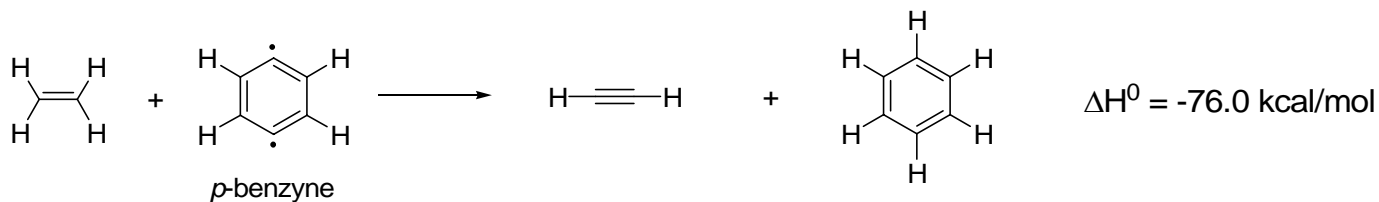


**Solution:** From Li to Cs, the metal becomes less electronegative and the C – M bond becomes more ionic. The hydrocarbon part resembles most the allyl anion when M = Cs. The conjugation is greatest, and so is the double bond character. This leads to increased barrier for rotation.

6. (5 pts) The two diradicals, **A** and **B**, shown below, exhibit very different properties. Diradical **A** is a singlet species (except for very high temperatures) while **B** is a triplet at all temperatures. Use resonance analysis to rationalize this difference.



7. (6 pts) The following reaction has been used to predict the standard heat of formation ( $\Delta H_f^0$ ) of *p*-benzyne, an important intermediate in the Bergman cyclization, which is a key step in the biological activity of the *enediynes antibiotics*. Use the *Benson* additivity tables to evaluate  $\Delta H_f^0$  of *p*-benzyne.



**Solution:** Using the Benson tables we can calculate the following:

$$\Delta H_f^0 \text{ of ethylene: } 2 \times 6.26 = 12.52 \text{ kcal/mol}$$

$$\Delta H_f^0 \text{ of acetylene: } 2 \times 26.93 = 53.86 \text{ kcal/mol}$$

$$\Delta H_f^0 \text{ of benzene: } 6 \times 3.30 = 19.80 \text{ kcal/mol}$$

The enthalpy of the reaction is the difference between the total enthalpy of formation of the products and that for the reactants. We know everything except  $\Delta H_f^0$  of *p*-benzyne (denoted as **X**).

$$\Delta H^0 = -76.0 \text{ kcal/mol} = 19.80 + 53.86 - 12.52 - \mathbf{X}$$

$$\mathbf{X} = 137.14 \text{ kcal/mol}$$