Problem Set 1: Review & Molecular Orbital Theory
Answers must be in the boxes provided to receive full credit. You may work in groups, but please turn in your own work.

1. Please label the hybridization of the nitrogen atoms in the molecules below.

   ![Chemical Structures]

   N in amides is trigonal planar!

2. (a) What is the molecular geometry of CH₃⁻: trigonal planar or trigonal pyramidal? (Circle your answer.)

   ![Molecular Geometry Diagram]

   (b) Draw both molecular orbital diagrams to explain your answer to part (a). You may ignore the core electrons and only show the orbitals where the valence electrons reside plus the LUMO (you do not need to show the higher, unoccupied molecular orbitals). Please illustrate the MO's as well as their relative energy levels. A Walsh diagram may be helpful.

   ![Molecular Orbital Diagrams]

   (c) Now consider CH₃⁻. Rationalize why it is trigonal pyramidal by comparing the appropriate molecular orbital diagrams.

   ![Rationalization Text]

   (d) See the Walsh Diagram in 2b for both conformations.

   - LUMO is lower in trig. pyramidal geometry due to orbital interaction between 2pz on C and 1s on all Hs. However, only occupied orbitals matter for relative energy.
   - HOMO is higher in trig. pyramidal geometry due to reduced orbital interactions.

   (e) For CH₃⁻, the 2pz orbital (see Walsh diagram above) becomes the HOMO; since molecular energy/stability is inferred by the HOMO, CH₃⁻ is more stable in trigonal pyramidal geometry.
3. (a) Using your "chemical intuition," please name and draw the HOMO and LUMO for the following molecules. Please put your answer in the table below.
   i) \( \text{CN}^- \)  
   ii) \( \text{H}_3\text{C}=\text{NH}_2^+ \)  
   iii) \( \text{H}_3\text{CBr} \)

(b) Now, in the table below, construct molecular orbital diagrams for each of the molecules. Clearly label the HOMO and LUMO in each MO diagram. You may ignore the core electrons and only show the orbitals where the valence electrons reside plus the LUMO (you do not need to show the higher, unoccupied molecular orbitals). Please illustrate the MO's as well as their relative energy levels.
More delocalized than in our "lone pair" but most electron density is on Br, as intuition told us.

4. Using Hückel MO Theory, please illustrate why the cyclopropenyl cation is stable, yet cyclobutadienyl cation is unstable.
5. Construct a Huckel MO diagram for hexatriene. Label the frontier molecular orbitals. Draw the molecular orbitals. Determine the energy of each MO in terms of \( \alpha \) and \( \beta \). Determine the coefficients of the atomic orbitals in the frontier molecular orbitals.

\[
\text{To determine } E: \\
E_j = \alpha + 2 \beta \cos \left( \frac{2\pi j}{n+1} \right) \\
E_6 = \alpha + 2 \beta \cos \left( \frac{6\pi}{6+1} \right) = \alpha + 1.8\beta \\
E_5 = \alpha + 2 \beta \cos \left( \frac{5\pi}{6+1} \right) = \alpha + 1.5\beta \\
E_4 = \alpha + 2 \beta \cos \left( \frac{4\pi}{6+1} \right) = \alpha + 1.2\beta \\
E_3 = \alpha + 2 \beta \cos \left( \frac{3\pi}{6+1} \right) = \alpha + 0.95\beta \\
E_2 = \alpha + 2 \beta \cos \left( \frac{2\pi}{6+1} \right) = \alpha + 0.5\beta \\
E_1 = \alpha + 2 \beta \cos \left( \frac{\pi}{6+1} \right) = \alpha + 0\beta \\
\]

\[
\text{To determine coefficients:} \\
C_{n6} = \left[ \frac{2}{(n+1)} \right]^\frac{1}{4} \sin \left[ \frac{n\pi}{6+1} \right] \\
\text{LUMO} \\
C_{n6} = 0.232 \\
C_{n5} = 0.522 \\
C_{n4} = 0.522 \\
C_{n3} = 0.698 \\
C_{n2} = 0.522 \\
C_{n1} = 0.522 \\
\]

6. (Grossman, Ch 1, #1d,f,g) Explain each of the following observations.

(a) Compound 1 has a much larger dipole moment than its isomer 2.

(b) Imidazole (3) is considerably more basic than pyridine (4).

(c) Fulvene (5) is electrophilic at the exocyclic C atom.

Similar to 6a:

not aromatic

not aromatic

aromatic

Nuc

major resonance structure
7. (Grossman, Ch 1, #2b,c,d,g,i,j) Please circle which of each pair of compounds is likely to be more acidic and explain why.

(a) Piperidinium is the conjugate acid of piperidine.
    Thus, compare the stabilities of their respective conjugate bases:
    \[ \text{neutral} \rightarrow \text{anionic} \rightarrow \text{stable} \]

(b) Ester is less electrophilic than ketone. Also, ester is electron-donating, which destabilizes the anion.

(c) \( (4n+2) = 10 \) aromatic \( n = 2 \)
    \( 4n = 12 \) anti-aromatic \( n = 3 \)

(d) Stabilized by resonance

(e) Can't resonate into \( \text{NO}_2 \) group

(f) Oxygen is more electronegative than nitrogen
8. (Grossman, Ch 2) Draw reasonable arrow-pushing mechanisms for the following reactions.

(a) \[ \text{Compound} \xrightarrow{\text{NaH}} \text{Product} \]

(b) \[ \text{Compound} \xrightarrow{\text{EtO}^-} \text{Product} \]

(many resonance structures possible)
(a) \[ \text{EtO}_2C\text{C}_{\text{Br}}\text{C}_{\text{Br}}\text{CO}_{\text{Et}} \xrightarrow{\text{KCN}, \text{EtOH}} \text{EtO}_2C\text{C}_{\text{Cl}}\text{C}_{\text{Br}}\text{CO}_{\text{Et}} \]

(b) \[ \text{EtO}_2C\text{C}_{\text{Br}}\text{C}_{\text{Br}}\text{CO}_{\text{Et}} \xrightarrow{1_{\text{p}} \rightarrow \sigma^*_{\text{C-Br}}} \text{EtO}_2C\text{C}_{\text{CN}}\text{C}_{\text{Br}}\text{Br} \]

(c) \[ \text{EtO}_2C\text{C}_{\text{Br}}\text{C}_{\text{Br}}\text{CO}_{\text{Et}} \xrightarrow{B} \text{EtO}_2C\text{C}_{\text{CN}}\text{C}_{\text{Br}}\text{Br} \]

(d) \[ \text{Carbene has a } 1_{\text{p}} \text{ and an empty } p\text{-orbital (acts as both a nucleophile and electrophile)} \]

\[ \text{Br}_{\text{Me}} \xrightarrow{\text{CHBr}_3, \text{sBuOK}} \text{Br}_{\text{Me}} \xrightarrow{\text{CH}_2\text{Li}} \]

\[ \text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3 \]

\[ \text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3 \text{ (gaseous \text{Li})} \]

\[ \text{LiBr} \xrightarrow{\text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3} \text{Br} \]

\[ \text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3 \]

\[ \text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3 \]

\[ \text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3 \]

\[ \text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3 \]

\[ \text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3 \]

\[ \text{Li} - \text{CH}_3 \text{ or Li}^+\text{CH}_3 \]
First part same as (e):

\[ \text{Reaction 1} \]

\[ \text{Reaction 2} \]

\[ \text{Reaction 3} \]