

SOLUTIONS

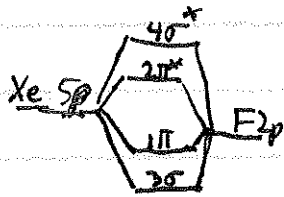
PROBLEM SET 10

CHM 3411, Dr. Chatfield

$$\epsilon_{F2p} < \epsilon_{Xe5p}$$

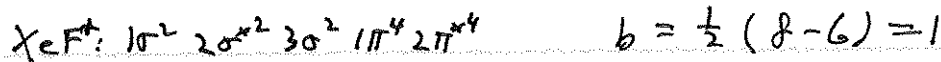
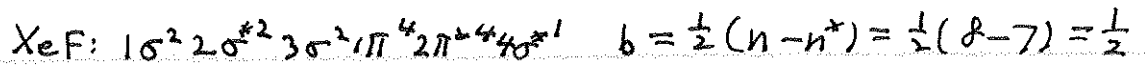
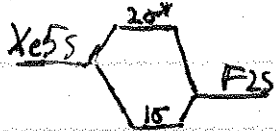
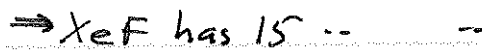


1.



$$I_F = 17.4 \text{ eV}, I_{Xe} = 12.1 \text{ eV}$$

Xe has 8 valence electrons



XeF^+ has the stronger bond, and hence the shorter bond.

2. The Pauling and Mulliken electronegativities are defined from experimental data

$$\chi_{\text{Mulliken}} = \frac{1}{2} (I + E_a)$$

χ_{Pauling} is determined from:

$$|\chi_A - \chi_B| = \left\{ D_0(\text{AB}) - \frac{1}{2} [D_0(\text{AA}) + D_0(\text{BB})] \right\}^{1/2}$$

The two scales are different, but they can be approximately interconverted using:

$$\chi_{\text{Pauling}} = 1.35 \chi_{\text{Mulliken}}^{1/2} - 1.37$$

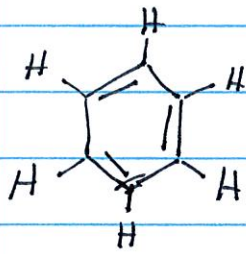
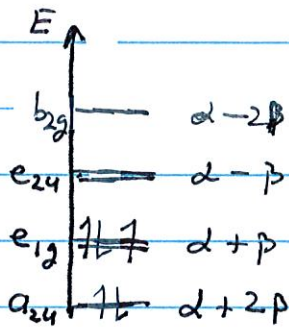
When Mulliken electronegativities are converted to the Pauling scale, the two can be compared.

From Table 10.1:

	<u>Pauling</u>	<u>Mulliken</u>	
Li	0.98	1.28	The agreement is pretty good but far from perfect. This underscores that electronegativity is a <u>construct</u> , not a directly observable property.
Be	1.57	1.99	
B	2.04	1.83	
C	2.55	2.67	
N	3.04	3.08	
O	3.44	3.22	
F	3.98	4.43	

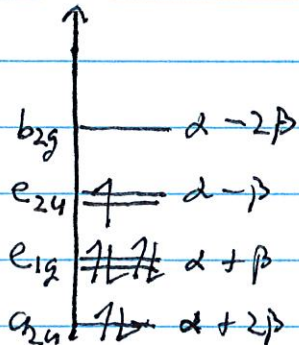
3.

benzene: each C has participates in:

3 σ bonds (using sp^2 hybrid orbitals)1 π .. (.. p orbital)
 \Downarrow
 6 π electrons total
benzene cation: 5 π -electronsconfiguration: $a_{2u}^2 e_{1g}^3$

$$E_{\pi} = 2(\alpha + 2\beta) + 3(\alpha + \beta) = 5\alpha + 7\beta$$

 \uparrow
 Energy of MO ($\alpha < 0, \beta < 0$)

 \uparrow
 π -electron binding En.
benzene anion: 7 π -electronsconfiguration: $a_{2u}^2 e_{1g}^4 e_{2u}^1$

$$E_{\pi} = 2(\alpha + 2\beta) + 4(\alpha + \beta) + (\alpha - \beta)$$

$$= 7\alpha + 7\beta$$

This is really the number
of electrons in the π system.

$$4. \quad \pi\text{-bond formation energy} = E_{bf} = E_{\pi} - N_c \alpha$$

$$\text{delocalization energy} = E_{de} = E_{\pi} - N_c (\alpha + \beta)$$

From earlier problem:

$$\text{benzene anion: } E_{\pi} = 7\alpha + 7\beta$$

$$\text{cation: } E_{\pi} = 5\alpha + 7\beta$$

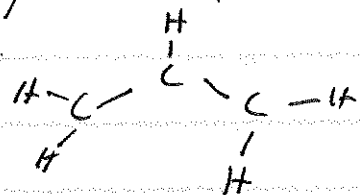
$$\text{Benzene anion: } E_{bf} = (7\alpha + 7\beta) - 7\alpha = 7\beta$$

$$E_{de} = (7\alpha + 7\beta) - 7(\alpha + \beta) = 0$$

$$\text{Benzene cation: } E_{bf} = (5\alpha + 7\beta) - 5\alpha = 7\beta$$

$$E_{de} = (5\alpha + 7\beta) - 5(\alpha + \beta) = 2\beta$$

6. allyl radical



This is the σ -bond framework.

Each carbon is sp^2 hybridized and, in addition, has one electron

in a p orbital. Thus each carbon contributes one p orbital to the π system. The Hückel equations are:

$$\psi = c_1 2p_{xA} + c_2 2p_{xB} + c_3 2p_{xC}$$

$$\begin{pmatrix}
 \alpha - E & \beta & 0 \\
 \beta & \alpha - E & \beta \\
 0 & \beta & \alpha - E
 \end{pmatrix}
 \begin{pmatrix}
 c_1 \\
 c_2 \\
 c_3
 \end{pmatrix}
 =
 \begin{pmatrix}
 0 \\
 0 \\
 0
 \end{pmatrix}$$

Multiplying by $\frac{1}{\beta}$ and defining $x = \frac{\alpha - E}{\beta}$, this becomes

$$\begin{pmatrix}
 x & 1 & 0 \\
 1 & x & 1 \\
 0 & 1 & x
 \end{pmatrix}
 \begin{pmatrix}
 c_1 \\
 c_2 \\
 c_3
 \end{pmatrix}
 =
 \begin{pmatrix}
 0 \\
 0 \\
 0
 \end{pmatrix}$$

Step 1 Solve for E in terms of α and β :

$$\begin{vmatrix}
 x & 1 & 0 \\
 1 & x & 1 \\
 0 & 1 & x
 \end{vmatrix}
 = 0 = x \begin{vmatrix}
 x & 1 \\
 1 & x
 \end{vmatrix} - 1 \begin{vmatrix}
 1 & 1 \\
 0 & x
 \end{vmatrix} + 0 \quad x = 0, \pm\sqrt{2}$$

$$\begin{matrix}
 \uparrow \\
 = x(x^2 - 1) - x = x^3 - 2x = x(x^2 - 2)
 \end{matrix}$$

$$x = \frac{\alpha - E}{\beta} \Rightarrow E = \alpha - x\beta$$

x	E
0	α
$+\sqrt{2}$	$\alpha - \sqrt{2}\beta$
$-\sqrt{2}$	$\alpha + \sqrt{2}\beta$

Step 2 Solve for c_1, c_2, c_3 for each value of E (or x)

The matrix eq. can be written as 3 eqs.

$$\begin{pmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$x c_1 + c_2 = 0$$

$$c_1 + x c_2 + c_3 = 0$$

$$c_2 + x c_3 = 0$$

Additionally, there is a normalization condition:

$$c_1^2 + c_2^2 + c_3^2 = 1 \quad (\text{because } S=0 \text{ in the Hückel approximation})$$

$x=0$ The equations above become:

$$(E=\alpha) \quad c_2 = 0, \quad c_1 = -c_3$$

From the normalization condition

$$2c_1^2 = 1 \quad c_1 = \frac{1}{\sqrt{2}}$$

$$c_1 = \frac{1}{\sqrt{2}} \quad c_2 = 0 \quad c_3 = -\frac{1}{\sqrt{2}} \quad (\text{or equivalently, } c_1 = -\frac{1}{\sqrt{2}} \quad c_2 = 0 \quad c_3 = \frac{1}{\sqrt{2}})$$

$$\boxed{X = +\sqrt{2}} \quad \textcircled{1} \quad \sqrt{2} c_1 + c_2 = 0$$

$$(E = \alpha - \sqrt{2}\beta) \quad \textcircled{2} \quad c_1 + \sqrt{2} c_2 + c_3 = 0$$

$$\textcircled{3} \quad c_2 + \sqrt{2} c_3 = 0$$

$$\textcircled{1} + \textcircled{3} \Rightarrow c_1 = c_3 \quad c_2 = -\sqrt{2} c_1$$

$$\text{norm: } c_1^2 + 2c_1^2 + c_1^2 = 1 \quad c_1 = \frac{1}{2}$$

$$c_1 = \frac{1}{2} \quad c_2 = -\frac{1}{\sqrt{2}} \quad c_3 = \frac{1}{2}$$

$$\boxed{X = -\sqrt{2}} \quad \textcircled{1} \quad -\sqrt{2} c_1 + c_2 = 0$$

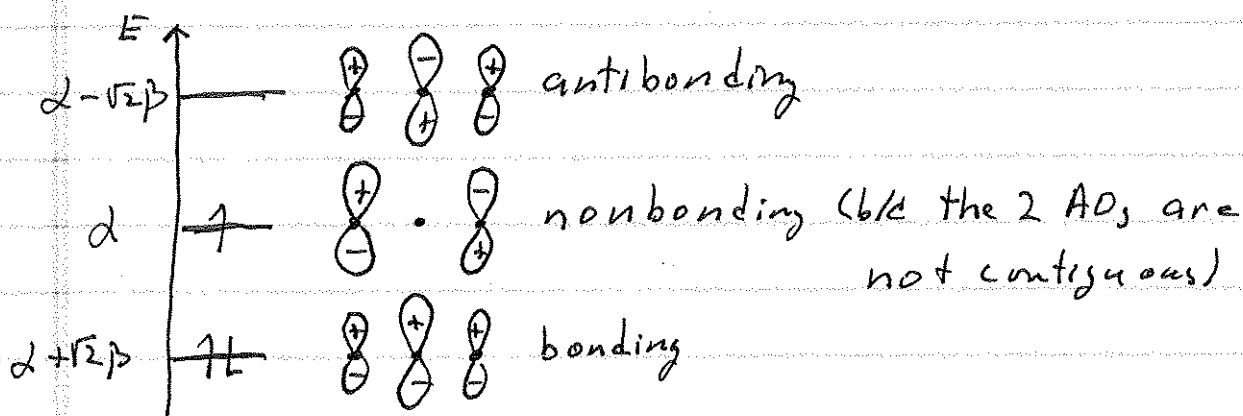
$$(E = \alpha + \sqrt{2}\beta) \quad \textcircled{2} \quad c_1 - \sqrt{2} c_2 + c_3 = 0$$

$$\textcircled{3} \quad c_2 - \sqrt{2} c_3 = 0$$

$$\textcircled{1} + \textcircled{3} \Rightarrow c_1 = c_2 \quad c_2 = \sqrt{2} c_1$$

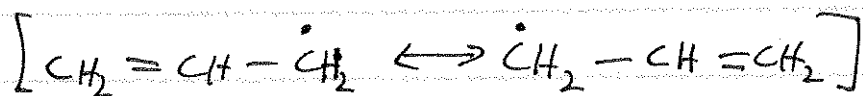
$$\text{norm: } c_1^2 + 2c_1^2 + c_1^2 = 1 \quad c_1 = \frac{1}{2}$$

$$c_1 = \frac{1}{2} \quad c_2 = \frac{1}{\sqrt{2}} \quad c_3 = \frac{1}{2}$$



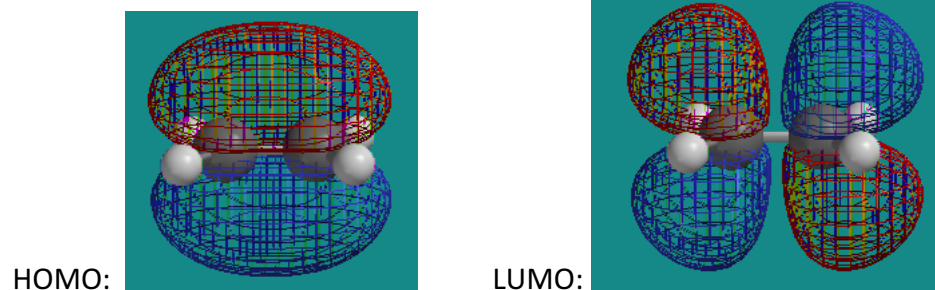
$$\text{Ground state energy} = 2(\alpha + \sqrt{2}\beta) + \alpha = 3\alpha + 2\sqrt{2}\beta = E_{\text{ground}}$$

We can trace the stability of the species to the fact that 2 electrons are in a bonding orbital and no electrons are in an antibonding orbital. There is also substantial delocalization. E_{π} is almost the same as if there were $1\frac{1}{2}$ π -bonds (a single π -bond has energy $2\alpha+2\beta$). This is why the allyl radical has surprisingly great stability in spite of being a radical. This picture is consistent with the more simplistic resonance-pair pictures.



7. Ethene modeled with Spartan

(A) At the HF/6-31G* level



Clearly, the HOMO is bonding and the LUMO is antibonding. In neutral ethane, the HOMO is filled and LUMO is empty.

	<u>C-C distance (Å)</u>
Neutral	1.317
Cation	1.403
Anion	1.435

Both the cation and the anion have a longer C-C distance than the neutral. This perfectly understandable. The cation has one fewer electron in the HOMO, a bonding orbital. The anion has an extra electron, in the LUMO, an antibonding orbital. Either way, bonding is decreased and hence bond length is increased.

(B) Ground-state energy of neutral ethane:

HF/6-31G* -78.031718 Hartree

HF/3-21G -77.600988 ..

The energy is smaller when calculated with the larger basis set (6-31G*). (Remember that the energies are negative, so larger magnitude means a smaller value.) This is consistent with the variational principle, which stipulates that the calculated energy will be greater than or equal to the true ground state energy. Generally, a larger basis set is able to give a wave function closer to the true wave function, and hence an energy closer to the true ground state energy.