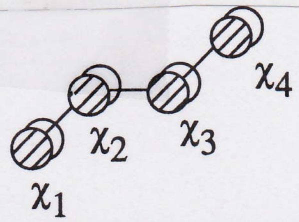
Answers - Chapter 12

1a.



$\chi_1$ & $\chi_4$ = basis 1
$\chi_2$ & $\chi_3$ = basis 2

| $C_{2h}$ | E | $C_2$ | i | $\sigma_h$ |  |
|---|---|---|---|---|---|
| $A_g$ | 1 | 1 | 1 | 1 |  |
| $B_g$ | 1 | -1 | 1 | -1 |  |
| $A_u$ | 1 | 1 | -1 | -1 |  |
| $B_u$ | 1 | -1 | -1 | 1 |  |
| $\Gamma_1$ | 2 | 0 | 0 | -2 | $b_g + a_u$ |
| $\Gamma_2$ | 2 | 0 | 0 | -2 |  |

|  | E | $C_2$ | i | $\sigma_h$ |
|---|---|---|---|---|
| $\chi_1$ | $\chi_1$ | $\chi_4$ | $-\chi_4$ | $-\chi_1$ |
| $\chi_2$ | $\chi_2$ | $\chi_3$ | $-\chi_3$ | $-\chi_2$ |

For basis 1:

$$\psi_{b_g} \propto (1)(\chi_1) + (-1)(\chi_4) + (1)(-\chi_4) + (-1)(-\chi_1)$$
$$\propto \chi_1 - \chi_4$$
$$\psi_{a_u} \propto (1)(\chi_1) + (1)(\chi_4) + (-1)(-\chi_4) + (-1)(-\chi_1)$$
$$\propto \chi_1 + \chi_4$$

For basis 1:

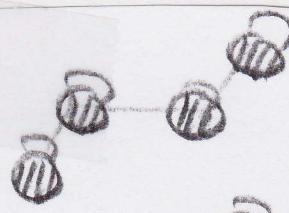
$$\psi'_{b_g} \propto (1)(\chi_2) + (-1)(\chi_3) + (1)(-\chi_3) + (-1)(-\chi_2)$$
$$\propto \chi_2 - \chi_3$$
$$\psi'_{a_u} \propto (1)(\chi_2) + (1)(\chi_3) + (-1)(-\chi_3) + (-1)(-\chi_2)$$
$$\propto \chi_2 + \chi_3$$

Taking SALC's from basis 1 & 2: $(\psi_{a_u} \pm \psi'_{a_u})$ & $(\psi_{b_{2g}} \pm \psi'_{b_{2g}})$

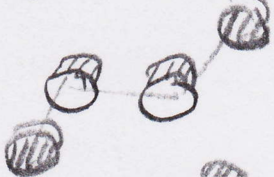
$\psi''_{a_u} \propto \chi_1 + \chi_2 + \chi_3 + \chi_4$ & $\psi'''_{a_u} \propto \chi_1 - \chi_2 - \chi_3 + \chi_4$

$\psi''_{b_g} \propto \chi_1 + \chi_2 - \chi_3 - \chi_4$ & $\psi'''_{b_g} \propto \chi_1 - \chi_2 + \chi_3 - \chi_4$

$\psi''_{1a_u} \equiv$

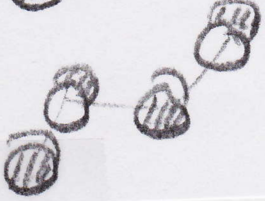


$\psi'''_{2a_u} \equiv$



$\psi''_{1b_g} \equiv$

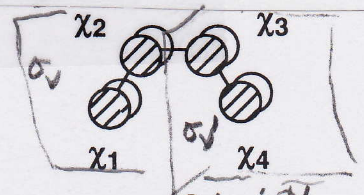
$\psi'''_{2b_g} =$



b) For 1,3-butadi-yne one can tell from the presence of vibrational structure in peaks ① & ② that they represent π ionizations. Both are stabilized by about 1eV with respect to peaks ① & ② in 1,3-butadiene. This is consistent with the fact that C≡C are shorter than C=C so the IP's in the former are larger than the latter. So the two peaks in butadiene must be from π ionizations

($1a_u$ & $1b_g$ as shown above).

2. a)



Basis 1: $\chi_1$ & $\chi_4$
Basis 2: $\chi_2$ & $\chi_3$

| | $E$ | $C_2$ | $\sigma_v$ | $\sigma_v'$ | |
|---|---|---|---|---|---|
| $\Gamma_1$ | 2 | 0 | -2 | 0 | $= a_2 + b_2$ |
| $\Gamma_2$ | 2 | 0 | -2 | 0 | $= a_2 + b_2$ |

| | $E$ | $C_2$ | $\sigma_v$ | $\sigma_v'$ |
|---|---|---|---|---|
| $\chi_1$ | $\chi_1$ | $-\chi_4$ | $-\chi_1$ | $\chi_4$ |
| $\chi_2$ | $\chi_2$ | $-\chi_3$ | $-\chi_2$ | $\chi_3$ |

For Basis 1

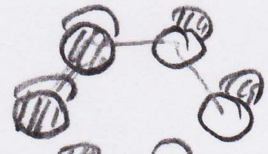
$$\psi_{a_2} \propto (1)\chi_1 + (1)(-\chi_4) + (-1)(-\chi_1) + (-1)(\chi_4)$$
$$\propto \chi_1 - \chi_4$$
$$\psi_{b_2} \propto (1)\chi_1 + (-1)(-\chi_4) + (-1)(-\chi_1) + (1)(\chi_4)$$
$$\propto \chi_1 + \chi_4$$

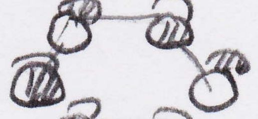
Likewise (It's easy to see the same form for Basis 2)

$$\psi'_{a_2} \propto \chi_2 - \chi_3$$
$$\psi_{b_2} \propto \chi_2 + \chi_3$$

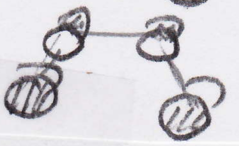
Now combining Basis 1 & 2:

\# nodes (along chain)

$\psi_{1a_2} \propto \chi_1 + \chi_2 - \chi_3 - \chi_4 =$  1

$\psi_{2a_2} \propto \chi_1 - \chi_2 + \chi_3 - \chi_4 =$  3

$\psi_{1b_2} \propto \chi_1 + \chi_2 + \chi_3 + \chi_4 =$  0

$\psi_{2b_2} \propto \chi_1 - \chi_2 - \chi_3 + \chi_4 =$  2

so energy ordering is:

$\psi_4 - \psi_{2a_2}$
$\psi_3 - \psi_{2b_2}$
$\psi_2 - \psi_{1a_2}$
$\psi_1 - \psi_{1b_2}$
$\uparrow$ P.E.

b)

For butadiene there are 4 π electrons so the occupation is

$\psi_2 \;\underline{\uparrow\downarrow}\; (\psi_{1a_2})$

$\psi_1 \;\underline{\uparrow\downarrow}\; (\psi_{1b_2})$

HOMO creates bond length differences

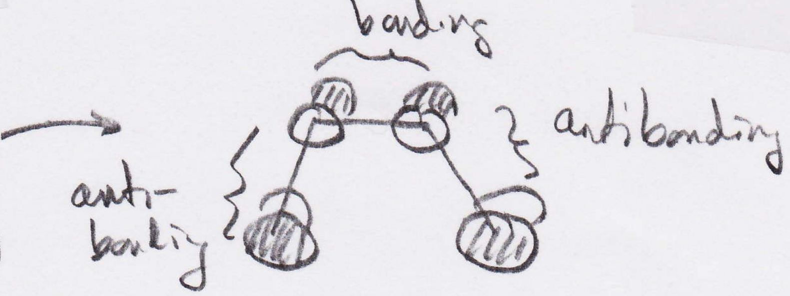
$\therefore \; d_1 = d_3 < d_2$

c) There are now 2 more π electrons

$\psi_3$ ⧺ ($\psi_{2b_2}$)

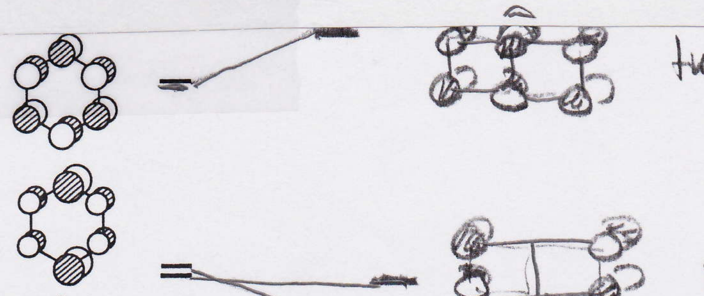
$\psi_2$ ⧺ ($\psi_{1a_2}$)

$\psi_1$ ⧺ ($\psi_{1b_2}$)



So now $d_1 = d_3 > d_2$
(or at least there is a tendency towards this from what happens in 2b)

3.


turn antibonding on.

remains nonbonding

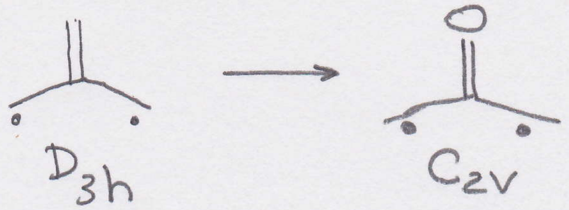
bonding turned on

antibonding turned on

remains nonbonding

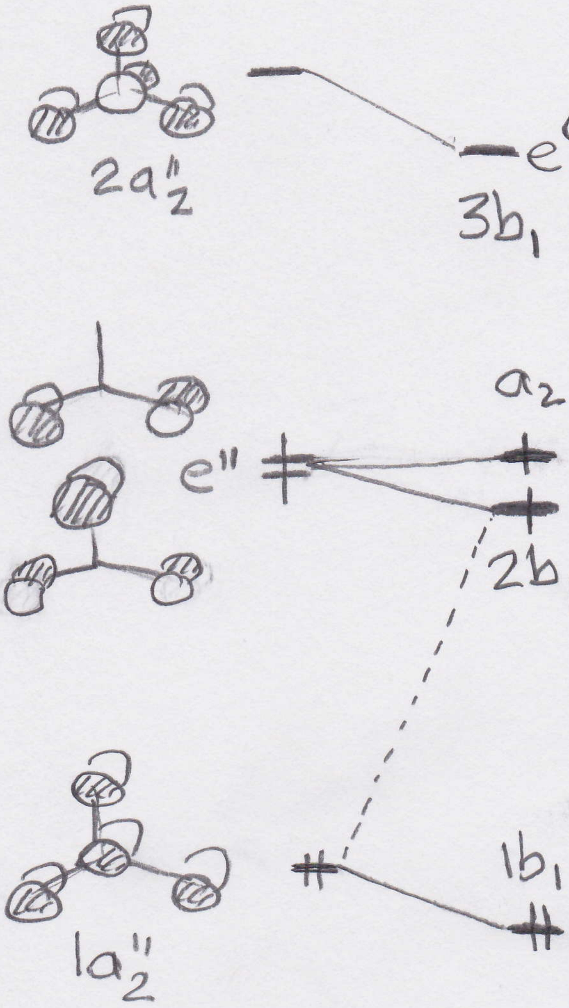
bonding turned on between AO's 1 & 4

4.



$\delta\alpha = (-)$ for replacing the one C for O

so for $1a_2''$, one member of $e''$ & $2a_2''$ $e^{(1)} = (+)(-) = (-)$



$3b_1$: $e^{(1)} = (-)$; $e^{(2)} = \frac{[(+)(+)(-)]^2}{(+)} = (+)$

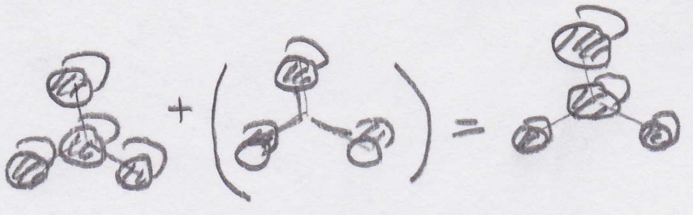
$a_2$: $e^{(1)} = e^{(2)} = 0$

$2b_1$: $e^{(1)} = (-)$; $e^{(2)} = \underbrace{\frac{[(+)(+)(-)]^2}{(+)}}_{\uparrow \text{ from } 1a_2''} + \underbrace{\frac{[(+)(+)(-)]^2}{(-)}}_{\uparrow \text{ from } 2a_2''}$

so $e^{(2)} \sim 0$

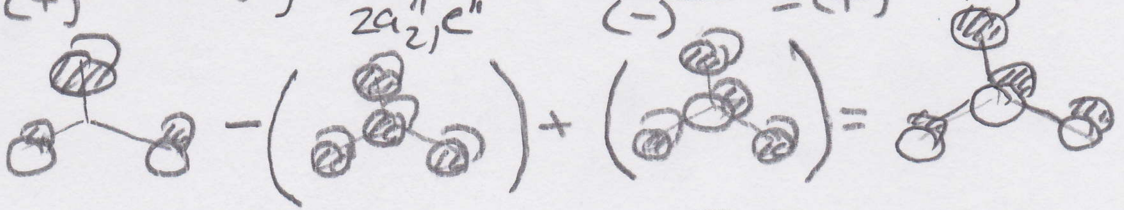
$1b_1$: $e^{(1)} = (-)$; $e^{(2)} = \frac{[(+)(+)(-)]^2}{(-)} = (-)$

$t^{(1)}_{e'',1a_2''} = \frac{(+)(+)(-)}{(-)} = (+)$ ∴



$t^{(1)}_{1a_2'',e''} = \frac{(+)(+)(-)}{(+)} = (-)$; $t_{2a_2'',e''} = \frac{(+)(+)(-)}{(-)} = (+)$

∴



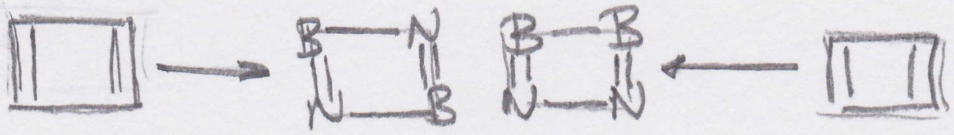
$t^{(1)}_{e'',2a_2''} = \frac{(+)(+)(-)}{(+)} = (-)$ ∴

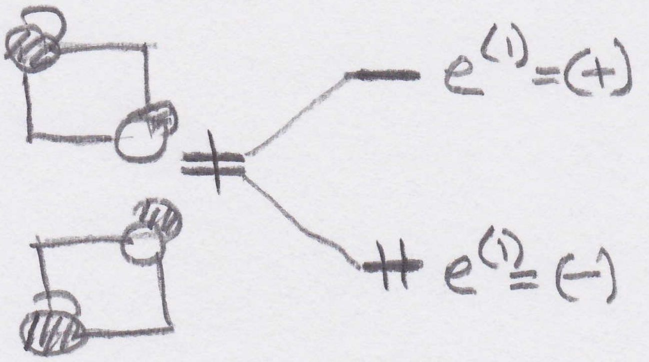
b) Structure A would be most consistent with an electron configuration

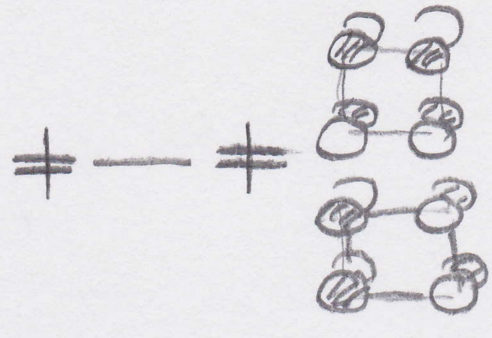
$$(1b_1)^2(2b_1)^1(a_2)^1 = {}^3B_1 \text{ or } {}^1B$$

For B: $(1b_1)^2(2b_1)^2(a_2)^0 = {}^1A_1$

5. Consider the electronegativity perturbation on starting from cyclobutadiene. Then $(\delta\alpha)_N = (-)$ and $(\delta\alpha)_B = (+)$. So for the $e_g$ set





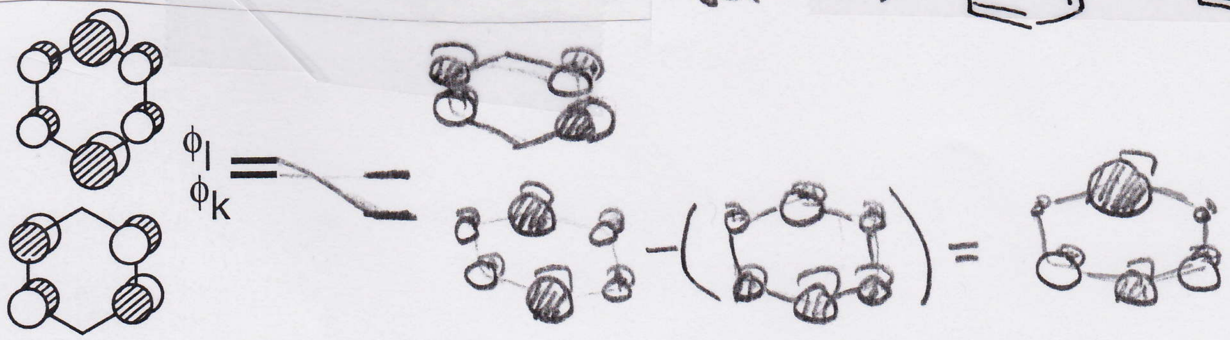


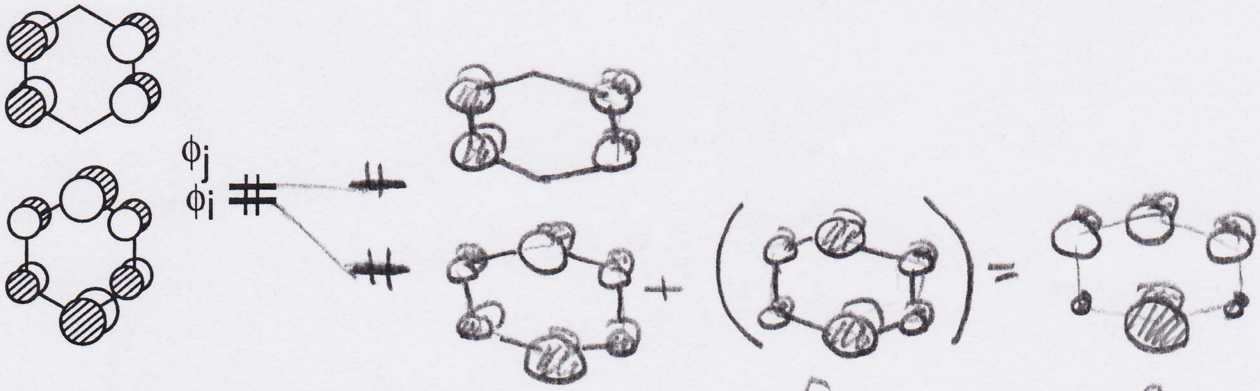
since $|\delta\alpha_N| \approx |\delta\alpha_B|$

then $e^{(1)} \approx 0$ for both

# 6. a)

$\delta\alpha = (-)$





$$e_i^{(1)} = (c_{\alpha i})^2(\delta\alpha) = (-)^2(-) = (-); \quad e_i^{(2)} = \frac{[(c_{\alpha i})(c_{\alpha \ell})\delta\alpha]^2}{e_i^0 - e_\ell^0} = \frac{(+)}{(-)} = (-)$$

$$t_{\ell i}^{(1)} = \frac{c_{\alpha i}\, c_{\alpha \ell}\, \delta\alpha}{e_i^0 - e_\ell^0} = \frac{(+)(+)(-)}{(-)} = (+)$$

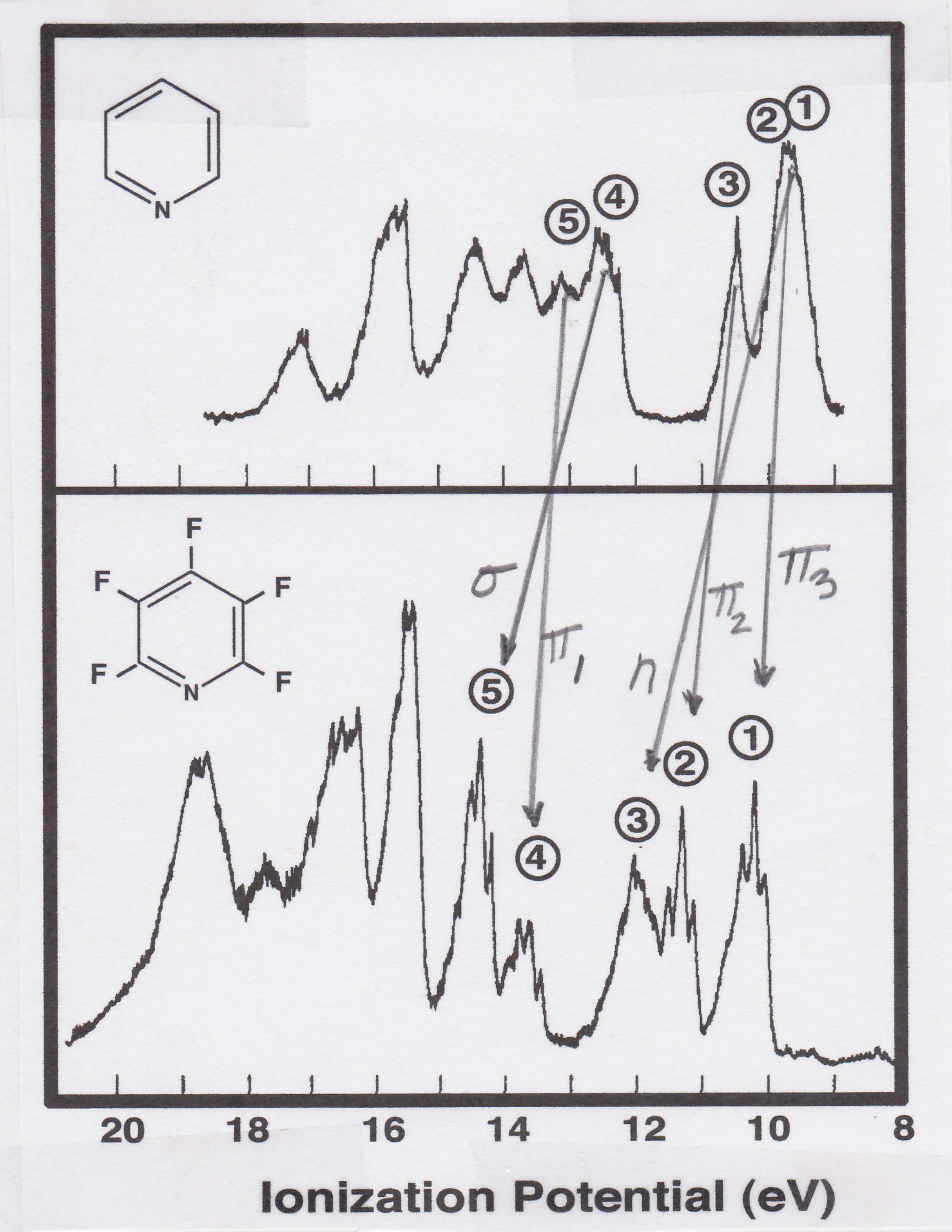
$$e_j^{(1)} = e_j^{(2)} = t_{ij}^{(1)} = \text{etc.} = 0 \qquad c_{\alpha j} = 0$$

$$e_k^{(1)} = e_k^{(2)} = t_{ik}^{(1)} = \text{etc.} = 0 \qquad c_{\alpha k} = 0$$

$$e_\ell^{(1)} = (c_{\alpha \ell})^2(\delta\alpha) = (-)^2(-) = (-); \quad e_\ell^{(2)} = \frac{[c_{\alpha \ell}\, c_{\alpha i}\, \delta\alpha]^2}{e_\ell^0 - e_i^0} = \frac{(+)}{(+)} = (+)$$

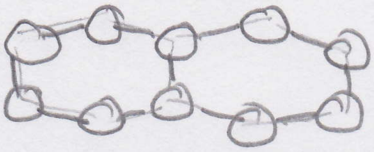
$$t_{i\ell}^{(1)} = \frac{c_{\alpha i}\, c_{\alpha \ell}\, \delta\alpha}{e_\ell^0 - e_i^0} = \frac{(+)(+)(-)}{(+)} = (-)$$

b) In pyridene the lone pair orbital, n, and 3 π orbitals are expected to be at low I.P.'s. The hint also indicates that there is one σ MO amoung the five. So two peaks must shift by ~ 2-3 eV and the others by a much smaller amount. The peak ①/② in $C_5H_5N$ then is probably n + $\pi_3$. peak ① in $C_5F_5N$ must be $\pi_3$. If peak ② in $C_5F_5N$ corresponds to n, the peak ③ in $C_5H_5N$ & $C_5F_5N$ is shifted too much for $\pi_2$. Thus, peak ③ must correspond in $C_5F_5N$ to n and peak ② (to peak ③ in $C_5H_5N$) to $\pi_2$. The shift of ④ in $C_5H_5N$ to peak ⑤ in $C_5F_5N$ is about right for a σ MO. This then leaves peak ⑤ in $C_6H_5N$ to correspond to peak ④ in $C_6F_5N$ which is $\pi_1$. This is plotted on the next page. Notice that $\pi_1$, $\pi_2$ and $\pi_3$ are all shifted by the same amount.

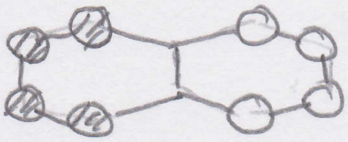


7. a) there are 10 π electrons in naphthalene so the lowest 5 MOs are filled; from a top view:

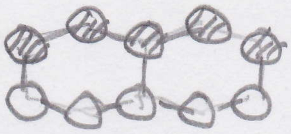
$\pi_1 =$



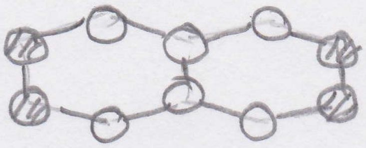
$\pi_2 =$



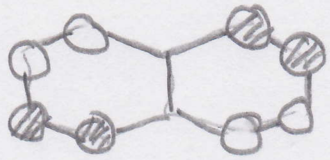
$\pi_3 =$



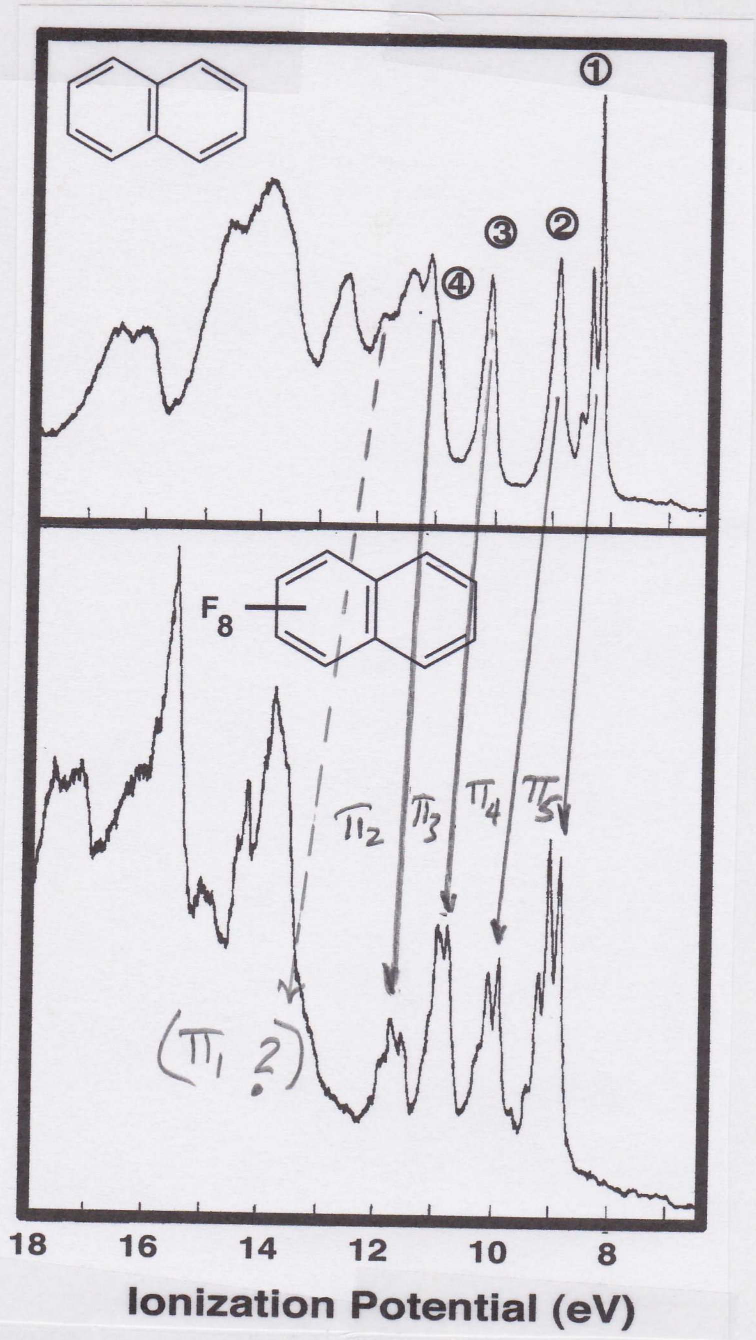
$\pi_4 =$



$\pi_5 =$



b) The correlation from $C_{10}H_8$ to $C_{10}F_8$ is pretty easy. The lowest four ionizations should correspond to $\pi_2$–$\pi_5$:



It is possible that $\pi_1$ is the peak at 12.0 eV which is then shifted a bit more to the shoulder indicated in $C_{10}F_8$

with $\beta = -2.2$ eV the best $\alpha = -7.0$ eV here are the calculated vs experimental IP's:

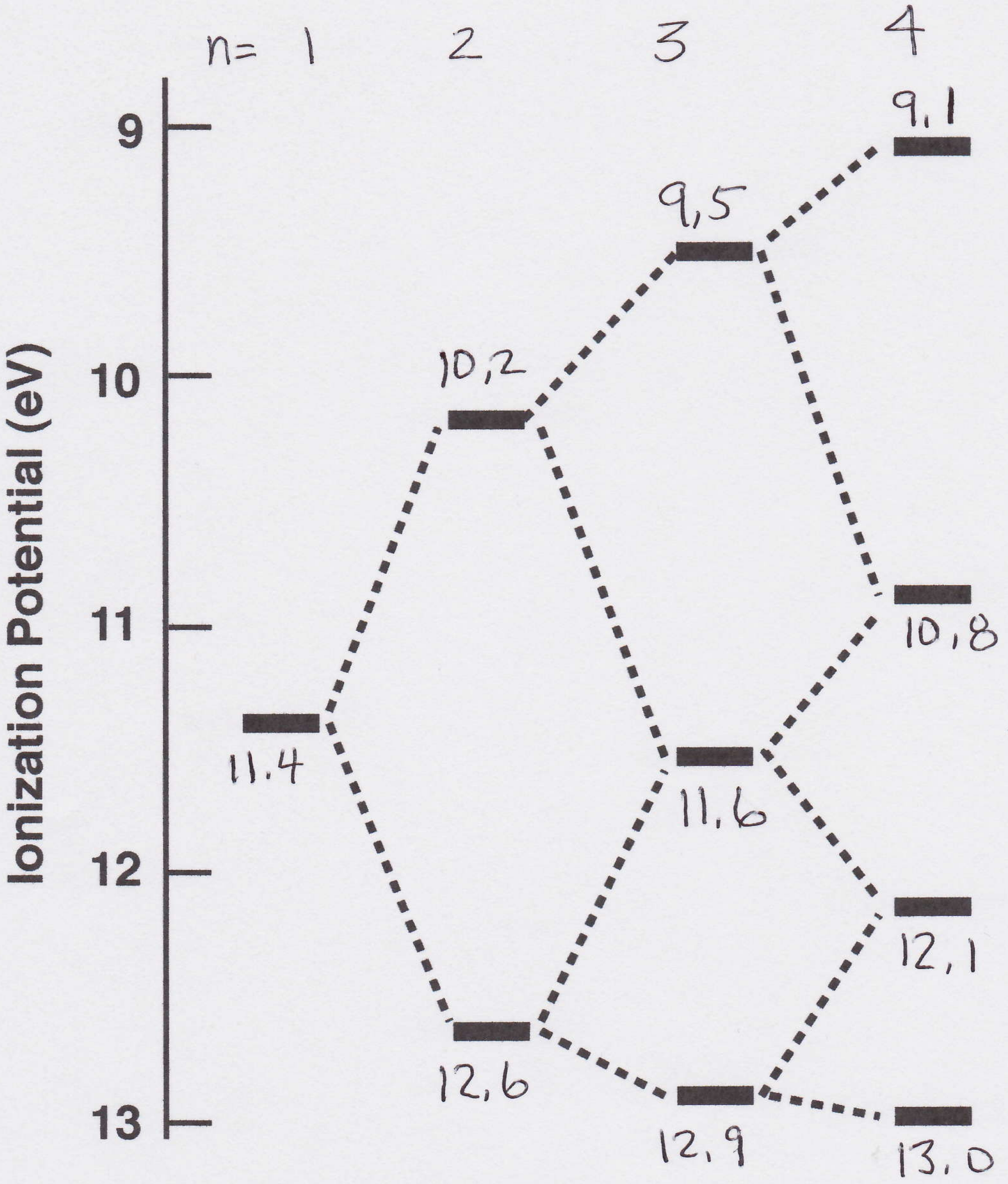
| | calc. | exp. (eV) |
|---|---|---|
| $\pi_5$ | 8.4 | 8.1 |
| $\pi_4$ | 9.2 | 8.8 |
| $\pi_3$ | 9.6 | 10.0 |

| | calc. | exp. (eV) |
|---|---|---|
| $\pi_2$ | 10.6 | 10.9 |
| $\pi_1$ | 11.8 | 12.0(?) |

* The correlation is really good for such a simple model!!

8.

$H(C\equiv C)_n - H$



what a great experimental verification of a theoretical model!