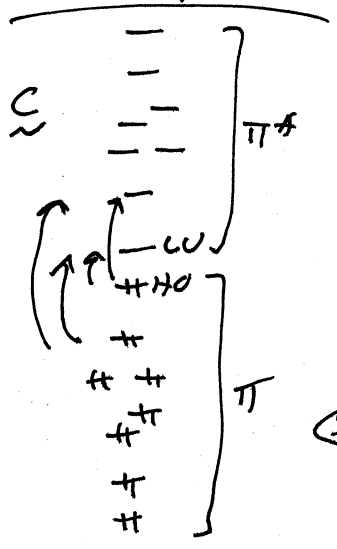
Chem 22 HW set 12 Graded

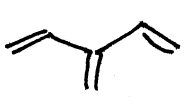
1. E: 250 nm ⇓ colorless; 114 kcal/mol
A: 400 nm abs purple ⇓ ∴ yellow; 72 kcal/mol
B: 540 nm abs green ⇓ ∴ red; 53 kcal/mol ⇒ ~40 kcal/mol ?
C: 715 nm ⇑ ~40 kcal/mol ↑ eye-ball estimate



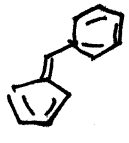
If this were the only transition the angel would appear green, but certainly other π → π* transitions would be possible at higher E ∴ likely on the visible.

715 nm is near-IR - if this is "broad", the abs would extend into the red.

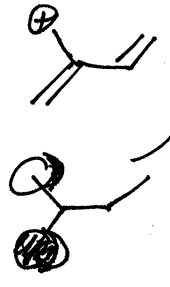
2.



LU E = α − 0,518β
HO E = α + 0,518β
∴ ΔE = 1,04β

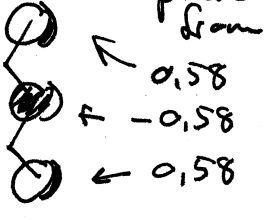


LU E = α − 0,178β
HO E = α + 0,618β
ΔE = 0,80β



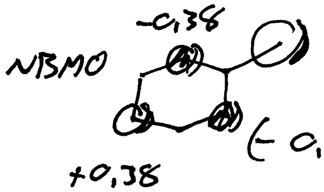
NBMO E = α
E = α + 0,765β
ΔE = 0,765β

3.



big surprise, eh?

← this is the amount of negative charge.



$(0{,}76)^2 = 0{,}58$ ← why so much + charge here?

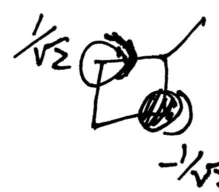
$(-0{,}38)^2 = 0{,}14$

same for each ring C

$(0,0,\beta)$ so total charge = +1 !

— charge positions are as predicted by res. structs !

— large amount of pos charge outside ring reflects the "desire" of the ring to maintain its aromatic cycle –

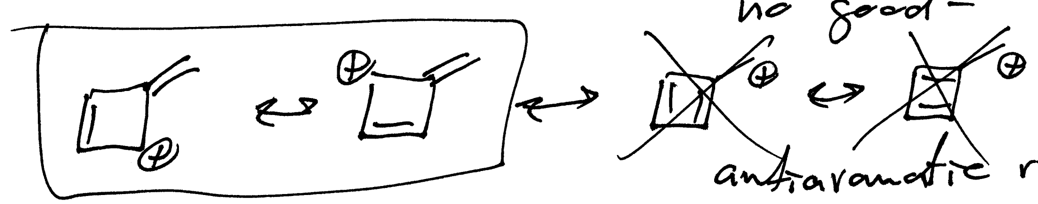


← NO p-orb coefficient ⇒ no charge here !

$-1/\sqrt{2}$ ⇒ ½ ⊕ on each ring C

⇓

no good –



antiaromatic ring !

— $\alpha - \sqrt{2}\beta$

— α

⥮ $\alpha + \sqrt{2}\beta$

$E_\pi = 2\alpha + 2{,}83\beta$

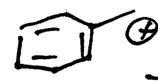
E_π(// + empty p) $= 2\alpha + 2\beta$

⇓

res E = $0{,}83\beta$

$(1{,}414\beta)$

(e) greater res stabiliz. ⇒ allyl Br should ionize faster!



— α

⥮ $\alpha + 1\beta$

⥮ $\alpha + 1{,}26\beta$

⥮ $\alpha + 2{,}10\beta$

$E_\pi = 6\alpha + 8{,}72\beta$

E_π(benzene + empty p) $= 6\alpha + 8\beta$

⇓

res E = $0{,}72\beta$