Today

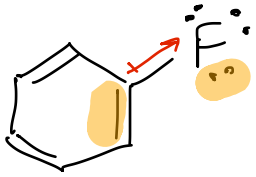
The affect of substituents on EAS
Activators, deactivators and o,p vs m Directors
Section 18.12, 18.13

Next Class

The affect of substituents on EAS
Activators, deactivators and *o*,*p* vs *m* Directors
Section 18.12, 18.13

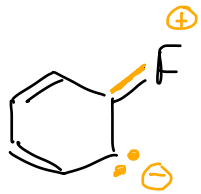
Please hand in reworked test 3 at the final on May 5

Reminder: final is on May 5 from 8:00 to 10:00



because F, Cl, Br, and I are electronegative

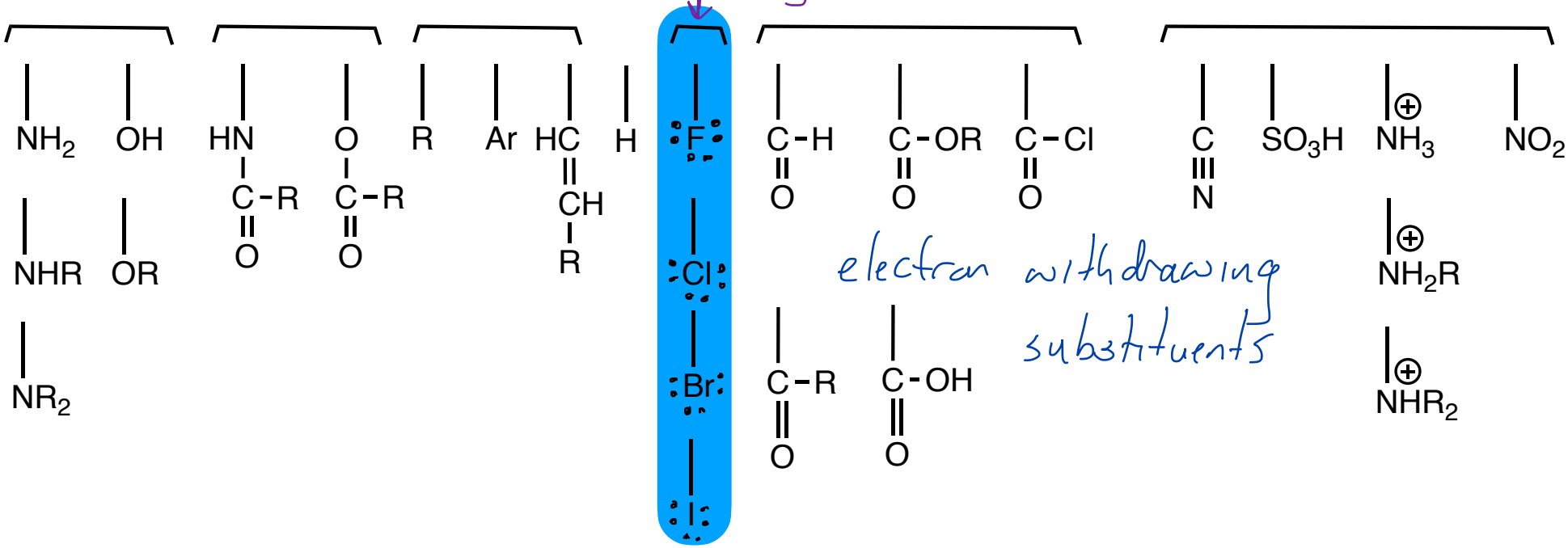
they are σ e⁻ withdrawing substituents

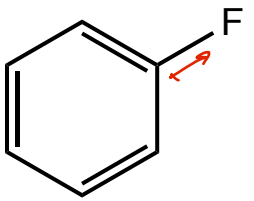


⊕ F atom?! Yeah, seems unlikely

they are weakly π e⁻ donating at best

σ withdrawing is stronger than π e⁻ donation so these are net e⁻ withdrawing

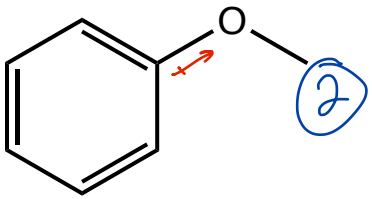




strongly σ withdrawing

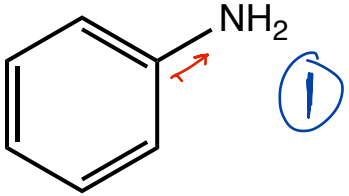
2p orbital on F ... good π interaction

too eneg for π donation to overcome eneg



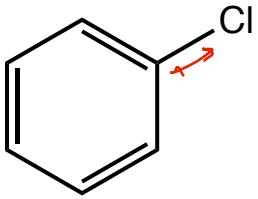
2p orbital on O ... good π interaction

slightly less good a π donation (as compared to N)



2p orbital on N ... good π interaction

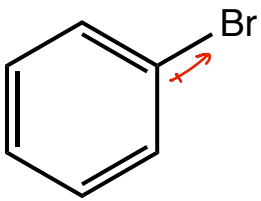
least eneg ... best π donor



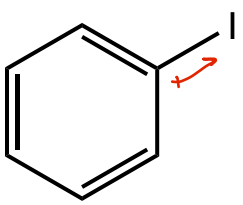
moderately σ withdrawing

if Cl has similar eneg to N, why isn't it activating?

Cl would have to use a 3p orbital to interact with benzene π system, the interaction is weak due to the orbital mismatch, so π donation cannot make up for the σ withdrawing ability of the atom.

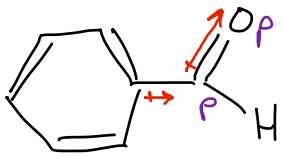


weakly σ withdrawing

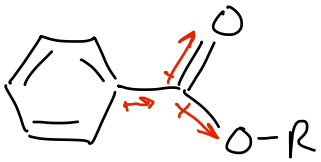


Activating and Deactivating a Benzene Ring toward EAS

Section 18.12



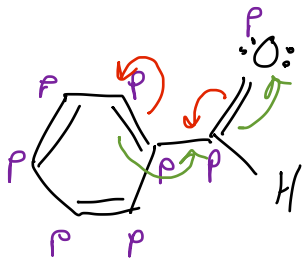
σ e⁻ withdrawing

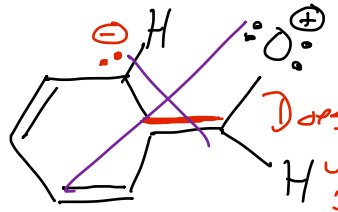


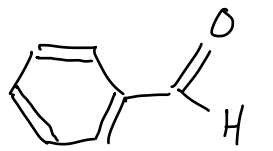
stronger σ
e⁻ withdrawing

charge sep
"inappropriate" charges
incomplete octet

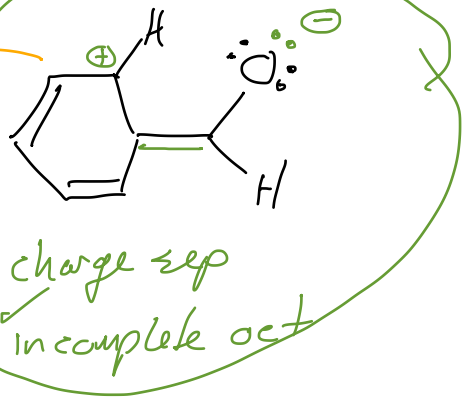
too many issues with this structure. Doesn't help us understand the molecule



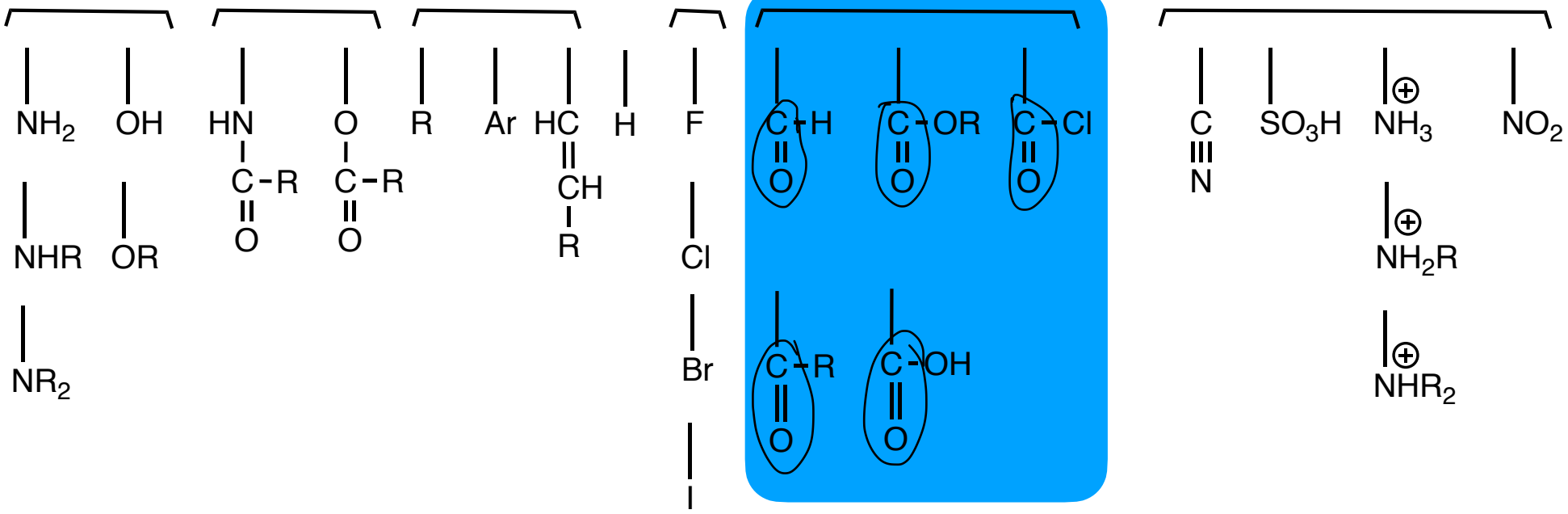


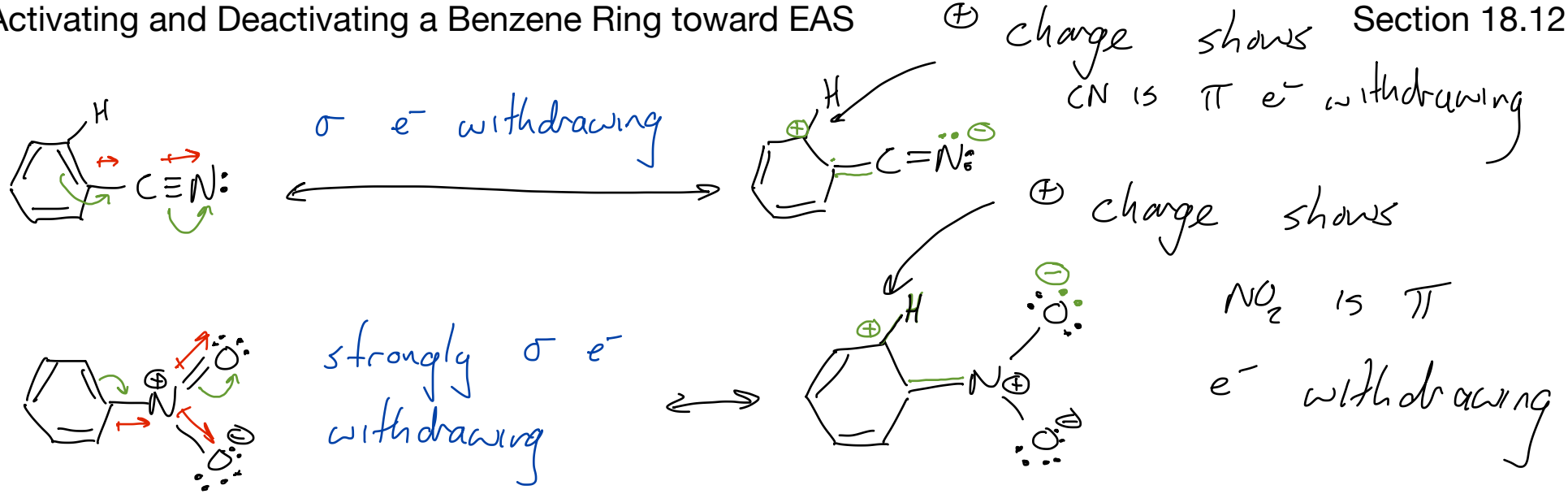


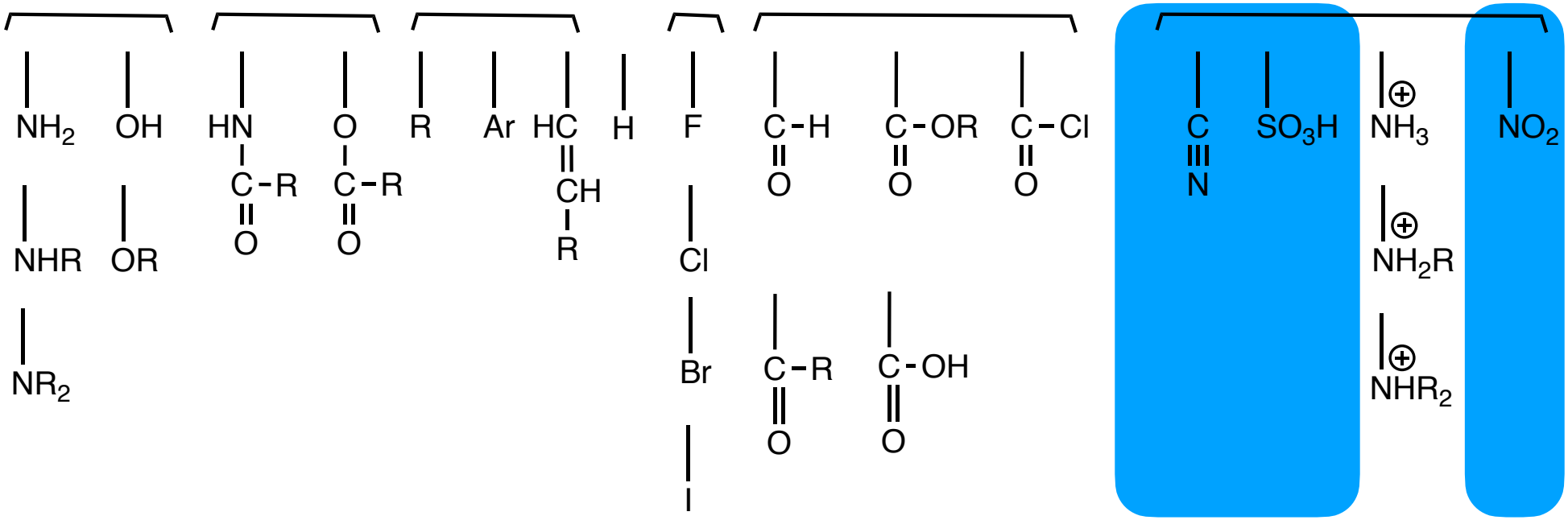
⊕ charge shows C=O is
π e⁻ withdrawing

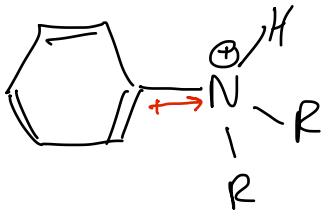


charge sep
incomplete oct



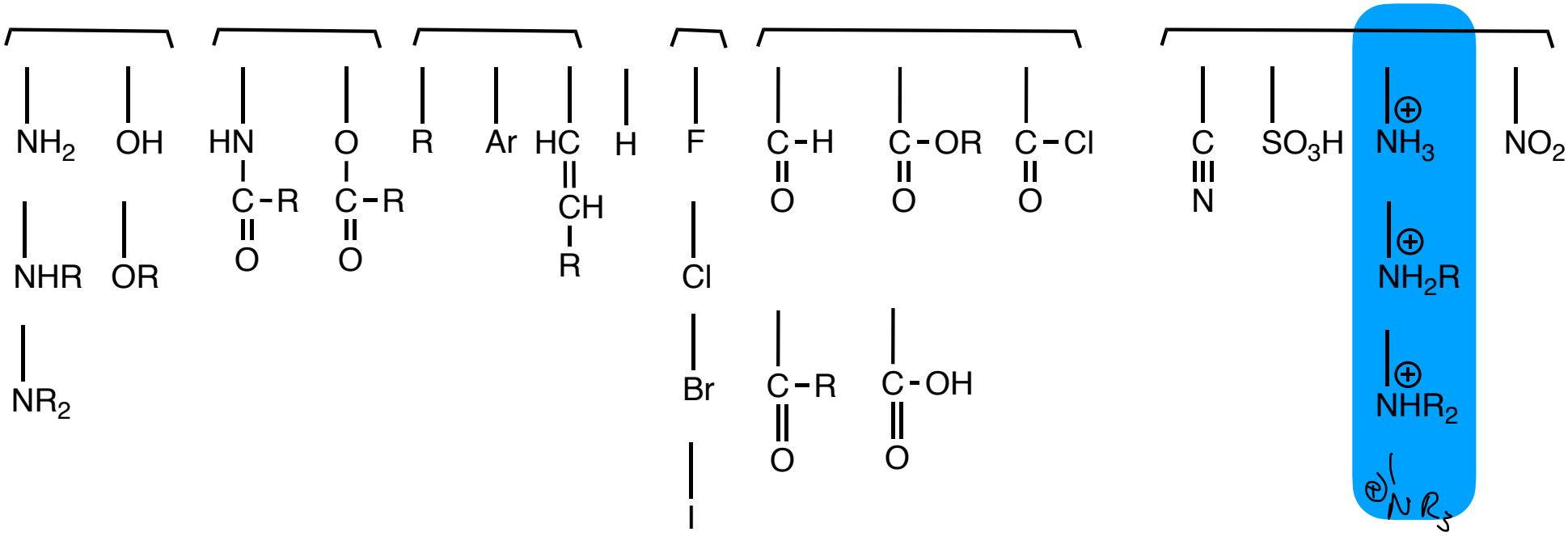

⊕ charge shows
CN is π e⁻ withdrawing
σ e⁻ withdrawing
⊕ charge shows
NO2 is π
e⁻ withdrawing
strongly σ e⁻
withdrawing

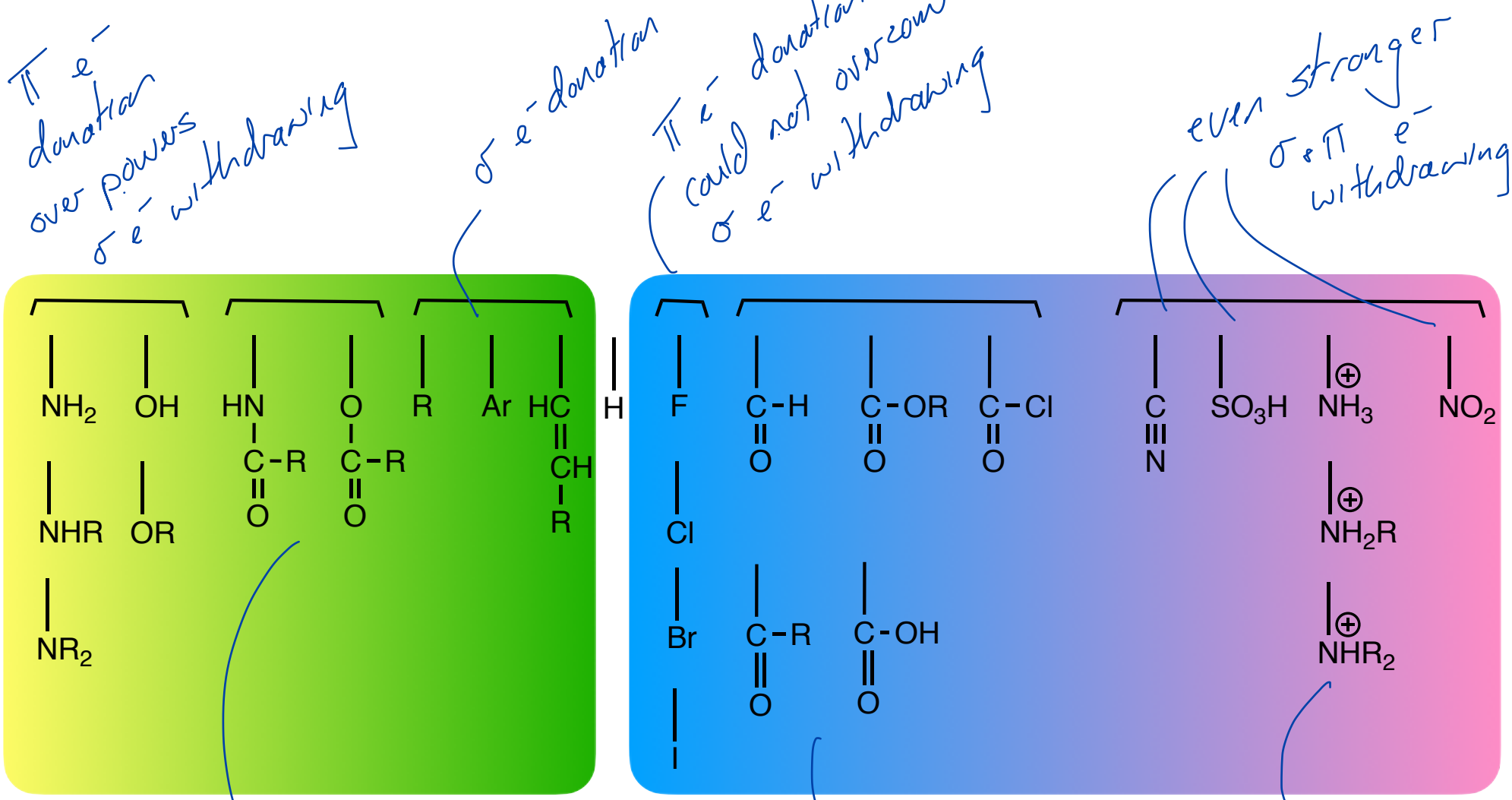

NH2
OH
NHR
OR
NR2
HN
C-R
O
O
C-R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C-H
O
C-OR
O
C-Cl
O
C-R
O
C-OH
O
C
N
SO3H
NH3
NH2R
NHR2
NO2



σ e⁻ withdrawing ... ⊕ charge on N makes it even more effective at withdrawing e⁻ density

no interaction with the π system




π e⁻ donation over powers σ e⁻ withdrawing
σ e⁻ donation
π e⁻ donation could not overcome σ e⁻ withdrawing
even stronger σ & π e⁻ withdrawing
NH2
OH
HN
O
R
Ar
HC
CH
R
NHR
OR
C-R
O
C-R
O
NR2
H
F
C-H
O
C-OR
O
C-Cl
O
C
N
SO3H
NH3
NO2
Cl
NH2R
Br
C-R
O
C-OH
O
I
NHR2
π e⁻ donation weakened by C=O group, but still enough to overcome σ withdrawing
C=O adjacent to benzene ring acts as σ & π withdrawing group
σ e⁻ withdrawing groups

relative to X, where is E?