

Example Question involving substituent effects (inductive vs resonance)

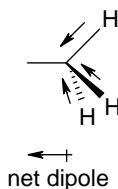
1. Interpret the following σ values in terms of the electronic character of each group. Discuss and explain the inductive and resonance effects. Show the resonance forms (if applicable). Compare/contrast the substituent pair in each row.

Substituent	σ_{meta}	σ_{para}	Substituent	σ_{meta}	σ_{para}
CH ₃	-0.07	-0.17	CF ₃	0.43	0.54
OCH ₃	0.07	-0.24	OCF ₃	0.40	0.35
NO ₂	0.71	0.78	CH=CH-NO ₂	0.32	0.26
OCOCH ₃	0.39	0.31	NHCOCH ₃	0.21	0

Solution:

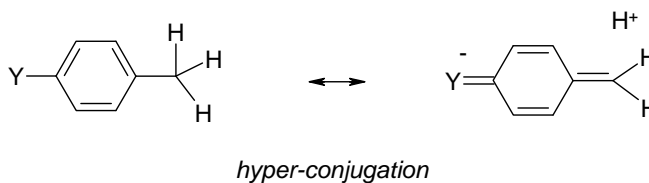
a) -CH₃ (methyl group)

Since carbon (EN = 2.5) is slightly more electronegative than hydrogen (EN = 2.2), there will be a small dipole moment pulling electron density away from hydrogen toward carbon. This slight build up of electron density on the carbon results in the methyl group having an electron donating effect by induction; note both σ_{m} and σ_{p} values are < 0 indicating methyl is EDG in both positions.



meta vs para

Since $\sigma_{\text{p}} = -0.17$ and $\sigma_{\text{m}} = -0.07$, we observe that a methyl substituent in the *para* position is more electron donating than in the *meta* position. Although there are no formal resonance contributions from the sp^3 hybridized carbon atom, there is a special type of resonance contribution known as *hyper-conjugation* which results in an additional electron donation associated with the *para*-methyl group.

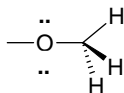


-CH₃ vs -CF₃

Replacing hydrogen atoms with the much more electronegative fluorine atom (EN = 4.0), results in electron withdrawing character as evidenced by the positive values for the substituent constants σ_{m} and σ_{p} . Again, *hyper-conjugation* explains the additional electron withdrawing power of the *para*-trifluoromethyl group.

b) $-\text{OCH}_3$ (methoxy group)

The methoxy group is electron withdrawing by the inductive effect of the oxygen atom, since the electronegativity of oxygen is 2.6. This is reflected in the positive value for σ_m .

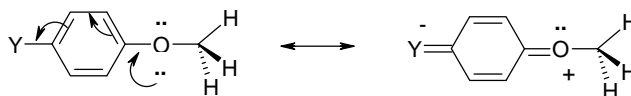


meta vs *para*

Recall that *meta* substituents only contribute inductive effects, whereas *para* substituents contribute both inductive and resonance effects. Thus, $\sigma_m \sim \sigma_I \sim 0.07$. In the *para* position, the lone pair of electrons on the oxygen can be donated back into the aryl ring by resonance giving rise to an additional resonance structure, shown below. Since $\sigma_p < 0$, the *para*-methoxy substituent is an EDG (even though the same group is an EWG in the *meta* position). Comparing the σ values for *meta* and *para*, we can see that the electron donating resonance effects (σ_R) dominate over the electron withdrawing inductive effect (σ_I).

Since $\sigma_p \sim \sigma_I + \sigma_R$,

we can estimate the $\sigma_R \sim -0.31$.



$-\text{OCH}_3$ vs $-\text{OCF}_3$

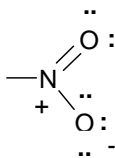
Replacing the hydrogens with fluorines results in a much more electron withdrawing substituent as can be seen by the positive values of σ_m and σ_p . Since $\sigma_p = 0.35$, we can see that in this case the inductive effect of $-\text{OCF}_3$ dominates over the resonance contribution.

$\sigma_m \sim \sigma_I \sim 0.40$

$\sigma_p \sim \sigma_I + \sigma_R, \therefore \sigma_R \sim -0.05$

c) -NO₂ (nitro group)

The nitro group is electron withdrawing via inductive and resonance effects as can be seen by the large positive σ values. The large inductive effect of NO₂ is the result of the formal + charge located on nitrogen. This electron deficiency withdraws electron density from the aryl ring.

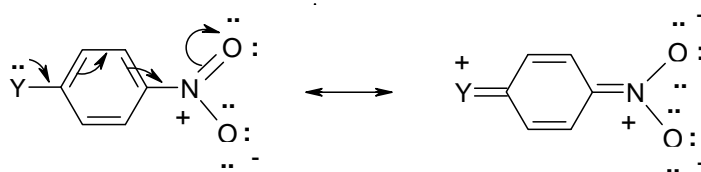


meta vs *para*

The difference in the substituent constants between *meta* and *para* positions is due to the additional resonance effect, which in this case is also electron withdrawing as can be seen in the resonance structure shown below.

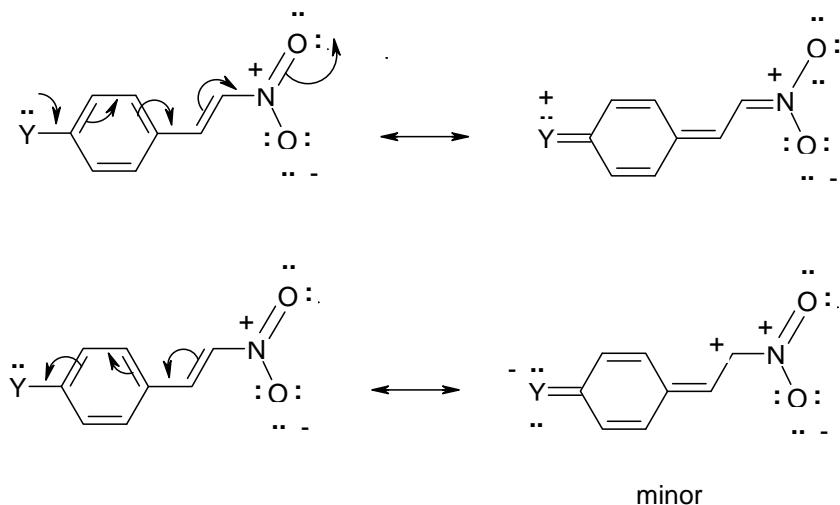
$$\sigma_m \sim \sigma_I \sim 0.71$$

$$\sigma_p \sim \sigma_I + \sigma_R, \therefore \sigma_R \sim 0.07$$



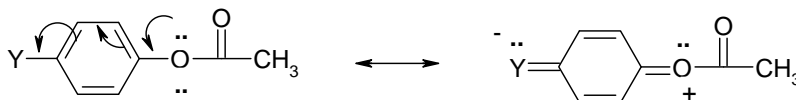
-NO₂ vs -CH=CH-NO₂

Adding an ethenyl group (-CH=CH-) between the aryl ring and the nitro group results in similar results. The substituent is still an EWG in either position ($\sigma > 0$), however the magnitude of the substituent constant is smaller since the nitro group is farther removed from the reactive centre. In the case of the *para*-CH=CH-NO₂ group, there is a slightly offsetting effect since the ethenyl group is electron donating by resonance.



d) $-\text{OCOCH}_3$ (alkyl ester group)

Since both σ_m and σ_p are positive, this substituent is electron withdrawing due to the electronegativity of the oxygen atom.

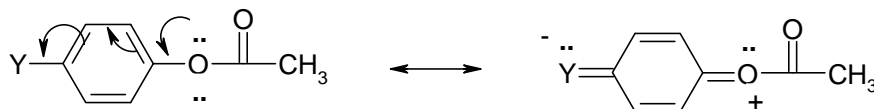


meta vs para

However, in the *para* position the lone pair electrons can be donated back through resonance (shown structure below).

$$\begin{aligned}\sigma_m &\sim \sigma_I \sim 0.39 \\ \sigma_p &\sim \sigma_I + \sigma_R, \therefore \sigma_R \sim -0.08\end{aligned}$$

Note that the electron donating resonance contribution in this case is considerably less than observed for $-\text{OCH}_3$ ($\sigma_R \sim -0.31$) due to the fact that the lone pair electrons on the ester are also delocalized out onto the carbonyl oxygen.



$-\text{OCOCH}_3$ vs $-\text{NHCOCH}_3$

The smaller electronegativity of nitrogen (EN = 3.0) relative to oxygen (EN = 3.5) results in smaller inductive electron withdrawing effect for the amide substituent versus the ester ($\sigma_m \sim \sigma_I \sim 0.21$). In the case of the *para* substituted amides, the electron withdrawing inductive effects are offset by an equal resonance electron donating effect to yield a resultant $\sigma_p = 0$. Thus, σ_R is roughly -0.21.