

I'm not robot



Electron donating withdrawing groups

Are phenyl groups electron donating or withdrawing. How to identify electron withdrawing and donating groups. Difference between electron withdrawing and donating groups. Electron withdrawing groups vs electron donating groups. Electron donating and withdrawing groups a level chemistry. Electron withdrawing and donating groups reddit. Are alkyl groups electron donating or withdrawing. Electron withdrawing and donating groups ocr a level chemistry. Electron donating and withdrawing groups chart. Electron donating and withdrawing groups examples. How to determine electron donating and electron withdrawing groups. Electron withdrawing and donating groups acidity. Electron donating and withdrawing groups mcat. Electron donating and withdrawing groups benzene. Electron withdrawing groups vs electron donating groups list.

Existing substituents on an aromatic ring can either speed up the reaction rate or influence where new groups attach during electrophilic substitution. Donor groups like hydroxyl (-OH) and amino (-NH2) share some of their electrons with the ring, making it more reactive. This is called activating, as these groups are often termed 'activating groups'. On the other hand, withdrawing groups like carbonyl (C=O) and halogens (F, Cl, Br) take away electron density from the ring, slowing down or blocking electrophilic reactions altogether. The positions where new groups are most likely to attach also depend on these electronic effects; donors usually direct attachment to ortho and para positions, while withdrawers prefer meta. This rule was first described by Crum Brown and Gibson in 1892 and is still known today as the Crum Brown-Gibson rule. Halogen substituents exhibit unique properties due to their electronegativity and non-bonding electrons. This leads to both inductive withdrawal and resonance donation, which compete with each other but ultimately result in meta directing groups for all halides except fluorine, which is an anomalous case. Fluorine exhibits a stronger resonance effect than the heavier halogens, making it an activating group at the para position while moderately deactivating the ortho and meta positions. Due to its strong electronegativity, iodine causes inductive withdrawal and directs comparably to the ortho and para positions. The magnitude of deactivation varies among substituents, with trifluoromethylsulfonyl groups being the strongest deactivators followed by haloformyl, carboxyl, and alkoxy carbonyl groups. Fluoro group is a weak deactivator at ortho and meta positions. Quantum mechanical analysis shows that formal charges in minor resonance contributors can predict directing effects of substituents. This understanding is crucial for determining the sites of reactivity in electrophilic aromatic substitution reactions, such as nitration. The competition between inductive withdrawal and resonance donation highlights the complexities of molecular interactions at the electronic level. In molecular orbital theory, a carbon atom with a higher coefficient is more likely to be attacked by an electrophile. This is because the larger coefficient enables better orbital overlap between the carbon and the electrophile. The perturbation of electron-withdrawing or electron-donating groups on a benzene ring can cause the π electron distribution to resemble that of an electron-deficient benzyl cation or electron-excessive benzyl anion, respectively. These species can be treated using Hückel theory, which predicts that the cation will withdraw electron density at ortho and para positions, favoring meta attack, while the anion will release electron density into these positions, activating them for attack. This is consistent with the predictions made by drawing resonance structures. For example, aniline has resonance structures featuring negative charges around the ring system, indicating a local electron excess that can donate electron density through resonance. As a result, attack occurs at ortho and para positions. In contrast, nitrobenzene has resonance structures featuring positive charges around the ring system, which withdraws electron density through resonance, favoring meta attack. Another argument considers the stabilization or destabilization of Wheland intermediates resulting from electrophilic attack at ortho/para or meta positions. The Hammond postulate then dictates that the relative transition state energies will reflect the differences in the ground state energies of the Wheland intermediates. These groups, including nitrobenzene and amino groups, exhibit both moderate to strong electron-withdrawing inductive effects (-I effect) and resonance effects (-M effect). As a result, they strongly deactivate the aromatic ring, making reactions proceed much slower compared to those in benzene. However, the resonance effect can dominate over the inductive effect, leading to these groups being electron-donating groups (EDGs) that are ortho/para directors. Phenol is an ortho/para director, but its reactivity increases in the presence of a base due to the higher reactivity of phenolate anion. The negative oxygen atom has an extra -I effect because it has a negative charge, which causes it to donate electron density to the carbons even at low temperatures. Fluorobenzene exhibits reactivity comparable to or even higher than that of benzene due to the combined effects of its functional groups. The negatively charged carboxylate ion moderately donates electrons, resulting in a weak electron-donating +I effect. However, this is partially countered by the stronger +M effect, which adds electron density back into the benzene ring through mesomeric interactions. This balance between -I and +M effects leads to strong para selectivity in electrophilic aromatic substitution reactions on fluorobenzene. The unique orbital overlap pattern, facilitated by the valence orbitals of fluorine being similar to those of carbon, contributes to this reactivity profile. Halogens attached to benzene, such as fluorobenzene and chlorobenzene, influence its reactivity. The farther apart orbital energies get, the less they can stabilize carbocations. Thus, chlorobenzene is less reactive than fluorobenzene due to weaker resonance donation but stronger inductive effect of chlorine compared to fluorine. However, bromo- and iodobenzenes are relatively more or as reactive as chlorobenzene because their lower electronegativities weaken both resonance and inductive effects. The overall order of reactivity is U-shaped with a minimum at chlorobenzene/bromobenzene. Halogenated benzenes react slower than benzene itself, but iodobenzene is less reactive than fluorobenzene due to its higher polarizability. Similar reasoning explains why phosphorus in phosphanes cannot donate electrons through induction and why hydroiodic acid is more acidic than hydrofluoric acid. Halogen groups are electron-donating and thus ortho/para directors. Nitroso group has a relatively strong -I effect but not as strong as the nitro group, and it has both +M and -M effects, with the latter being more favorable. This makes the nitroso group less available to donate electrons but still capable of donating during the Wheland intermediate formation, making it an ortho/para director. The effect is illustrated in electrophilic aromatic substitutions with alkyl substituents of different sizes for nitration reactions. Substrate toluene ethylbenzene cumene tert-butylbenzene ortho product 58% 45% 30% 16% meta product 5% 6% 8% 11% para product 37% 59% 62% 73% The ratio of ortho to para products is 1.57:1, 0.76:1, 0.48:1, and 0.22:1 respectively. This shows that the methyl group in toluene is small, favoring the ortho product, while the t-butyl group is large, resulting in a para product as the major one. In contrast, even toluene has a less-ortho product ratio than expected. When multiple substituents are present on the ring, the third substituent's location can be relatively predictable, especially if the existing substituents reinforce or create symmetry. Otherwise, the most activating substituent typically controls over the less activating one. Substituents often add ortho to amines and amides, with ortho/meta directors controlling over meta ones. When multiple substituents are equally activating, steric hindrance dominates regioselectivity, leading to para substitution to either existing group in meta-chlorotoluene. Fluorobenzene was found to be anomalous in its reactivity towards electrophilic aromatic substitution by Rosenthal and Schuster in their 2003 study. The phenomenon was further explored in Jonathan Clayden's Organic Chemistry, which noted the unusual behavior of fluorobenzene. Andrew Abell et al.'s synthesis of ring-deactivated deuterated (hydroxymethyl)pyrroles also shed light on related phenomena. Vollhardt's Organic Chemistry: Structure and Function provided a comprehensive overview of these processes. Other notable studies include "Substitution Reactions of Benzene Derivatives" by LibreTexts, David Lewis' Advanced Organic Chemistry, Ian Fleming's Frontier Orbitals and Organic Chemical Reactions, Francis Carey's Organic Chemistry, and Peter Sykes' Some Organic Reaction Pathways. These sources collectively contributed to a deeper understanding of electrophilic aromatic directing groups and their effects on benzene derivatives.