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Atomic Charge Reveals Global Electron Redistribution in Substituted Benzene: A Semiempirical Quantum Study

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ABSTRACT

This study investigates how the electron donating substituents affect the charge at C_0 in substituted benzene systems, using the AM1 semiempirical method in ORCA. Aromatic systems exhibit complex electron density redistribution governed by π-electron delocalization, where substituent effects propagate across the entire ring rather than remaining localized. The research modeled eleven benzene derivatives covering alkyl, amino, and oxygen-containing groups, then compared charge changes at C_0 against unsubstituted benzene using both Mulliken and Löwdin population analyses. The results reveal that electron-donating groups do not necessarily increase electron density locally at the C_0; instead, the donated electron density is redistributed throughout the aromatic π-system. The amino groups exhibit moderate influence through resonance interactions without significant localization at C_0, while a minimal charge variation, indicating weak inductive effects was provided by Alkyl substituents Phenol and alkoxy derivatives perturb the ring more noticeably because the lone pairs donate effectively into the π-system. The anomalous behavior was displayed by ethoxybenzene , a suggesting the ethyl chain adds an inductive contribution on top of the resonance effect from oxygen. Despite differences in absolute values, both population analysis methods produce consistent trends, supporting the robustness of the findings. Overall, this study highlights that ΔC_0 serves as an indicator of global electron redistribution rather than localized charge accumulation, providing a more physically meaningful interpretation of substituent effects in aromatic systems.

Keywords: aromatic systems, atomic charge, electron redistribution, electron-donating groups, substituent effects

ABSTRAK

Penelitian ini mengkaji pengaruh elektronik dari substituen pendonor elektron terhadap C_0 pada sistem benzena tersubstitusi menggunakan pendekatan kimia komputasi. Sistem aromatik menunjukkan redistribusi kerapatan elektron yang kompleks akibat delokalisasi elektron π, di mana efek substituen menyebar ke seluruh cincin, bukan hanya terlokalisasi pada satu posisi. Untuk mengevaluasi fenomena ini secara sistematis, sebelas turunan benzena yang mewakili substituen alkil, amino, dan oksigen dimodelkan dan dianalisis menggunakan metode semiempiris AM1 dalam program ORCA. Variasi muatan atom pada posisi C_0 dihitung relatif terhadap benzena dan dianalisis menggunakan metode populasi Mulliken dan Löwdin untuk memastikan konsistensi hasil. Hasil penelitian menunjukkan bahwa gugus pendonor elektron tidak selalu meningkatkan kerapatan elektron secara lokal pada karbon

ipso, melainkan mendistribusikan elektron ke seluruh sistem π aromatik. Substituen alkil menunjukkan perubahan muatan yang kecil, mencerminkan efek induktif yang lemah, sementara gugus amino memberikan pengaruh sedang melalui interaksi resonansi tanpa akumulasi muatan yang signifikan pada C_0. Substituen oksigen, khususnya fenol dan turunan alkoksi, menunjukkan efek elektronik yang lebih kuat akibat sumbangan pasangan elektron bebas melalui resonansi. Menariknya, etoksibenzena menunjukkan perilaku anomali yang mengindikasikan kombinasi efek resonansi dan kontribusi induktif tambahan dari rantai alkilnya. Meskipun terdapat perbedaan nilai absolut, kedua metode analisis menunjukkan tren yang konsisten, sehingga memperkuat keandalan hasil penelitian. Secara keseluruhan, ΔC_0 dapat dipahami sebagai indikator redistribusi elektron global, bukan sekadar akumulasi muatan lokal, sehingga memberikan interpretasi yang lebih bermakna terhadap efek substituen dalam sistem aromatic

Kata kunci: sistem aromatik; muatan atom; redistribusi elektron; gugus pendonor elektron; efek substituen

INTRODUCTION

The electronic behavior of aromatic systems is fundamentally tied to how π-electrons are delocalized across the molecular framework, a quantum mechanical outcome of orbital overlap that lowers overall system energy (Máximo-Canadas et al., 2025). From a computational physics perspective, the aromatic ring behaves as a coupled electronic system, where any perturbation introduced by a substituent propagates throughout the entire π-network. The substituent effects should be interpreted as global electronic responses rather than purely local phenomena Atomic charge is commonly used to track these redistributions of electron density, even though it is ultimately a mathematical construct derived from partitioning the electron density function, not a directly measurable quantity (Galabov et al., 2022).

In substituted benzene, the carbon directly bonded to the substituent (C_0) is particularly sensitive to electronic perturbation. The inductive effects through σ-bonds and resonance interactions within the π-system results the charge reflects of the interplay Conventionally, electron-donating groups (EDGs) such as $–NH_2$, –OH, and alkoxy substituents are expected to increase electron density, while alkyl groups contribute more weakly via inductive donation (Verma et al., 2023). The new research finds that the electron density change is not confined to C_0 but spread across the ring as part of a collective electronic adjustment that maintains aromatic stability (Szatylowicz et al., 2019). Although state-of-the-art computational approaches, including NICS, EDDB, GIMIC, and molecular electrostatic potential (MESP), provide detailed insights into aromaticity and charge distribution (Krishnapriya & Suresh, 2023; Patra et al., 2023) ,they primarily describe global properties and often yield inconsistent interpretations in substituted systems, leaving the relationship between local charge descriptors and overall electronic behavior insufficiently clarified. Although previous studies have explored substituent effects and charge distribution, the relationship between local atomic charge variations at positions such as C_0 and global electron redistribution remains insufficiently clarified, particularly across different population analysis methods. This study does not aim to introduce a new computational method, but rather to provide a clearer conceptual interpretation of how local atomic charge variations reflect global electron redistribution in aromatic systems. Therefore, this study analyzes the effect of electron-donating substituents on the C_0 atomic charge using both Löwdin and Mulliken population analyses, enabling cross-validation of electronic trends while minimizing methodological bias;

importantly, the variation of ΔC_0 relative to benzene is employed as a quantitative measure, providing a more physically consistent interpretation that directly links local charge variation to global electron redistribution within the aromatic π-system.

METHODOLOGY

All calculations were performed in silico on a Windows 11 64-bit system using a laptop equipped with an Intel® Core™ i7-10510U processor (2.30 GHz), 16 GB RAM, 128 MB graphics, and a 1 TB SSD. Molecular structures of eleven benzene derivatives representing electron-donating groups (toluene, ethylbenzene, isopropylbenzene, tert-butylbenzene, aniline, N,N-dimethylaniline, p-toluidine, phenol, benzyl alcohol, anisole, and ethoxybenzene) were constructed using ACD/ChemSketch and pre-optimized and visualized in Avogadro. Benzene was used as the reference system for all comparisons.

Quantum chemical calculations were carried out using ORCA. Geometry optimization and electronic structure calculations were performed using the semiempirical AM1 method under identical computational conditions for all molecules to ensure consistency. The ORCA input was defined using the keyword:

! AM1 Opt

Atomic charge analysis was performed using both Mulliken and Löwdin population schemes to evaluate electron density redistribution. The ipso carbon (C_0), defined as the aromatic carbon directly bonded to the substituent, was selected as the primary probe of substituent-induced electronic effects . The variation in atomic charge (ΔC_0) was calculated relative to benzene using:

$$\Delta C_0 = C_0(\text{substituted}) - C_0(\text{benzene})$$

to quantify the electronic perturbation introduced by each substituent. In addition, the average atomic charge of the remaining aromatic carbons (C1–C5) was calculated to represent the overall redistribution of electron density within the π-system.

All calculated data were processed and visualized using Microsoft Excel to generate bar charts and correlation plots, allowing comparison between Löwdin and Mulliken results and identification of substituent-dependent trends.

RESULTS AND DISCUSSION

The Effect of Electron-Donating Substituents on the C_0 Atomic Charge

Throughout this study, C_0 denotes the aromatic carbon bonded directly to the substituent. Charge variations at this position were examined to assess how EDGs modify the electron density distribution of the ring, given that substituent-induced inductive and resonance effects are expected to be most directly registered at the point of attachment.

Benzene served as the reference system, yielding atomic charges of −0.130125 (Löwdin) and −0.191718 (Mulliken population analysis) , values against which charge shifts in each substituted derivative were compared. All calculations were carried out at the semiempirical AM1 level, applied uniformly across the full set of compounds. Differences the observed variations in the C_0 atomic charge can be attributed primarily to the intrinsic electronic characteristics of the substituents rather than methodological differences.

Table 1. ΔC_0 Atomic Charge Variation of Substituted Benzene Derivatives Based on Löwdin and Mulliken Population Analyses

No	Compound	ΔLöwdin Charge (C_0)	ΔMulliken Charge (C_0)
1	Toluene	-0.004662	-0.066019
2	Ethylbenzene	0.002663	-0.058144
3	Isopropylbenzene	0.000129	-0.082609
4	tert-Butylbenzene	0.008573	-0.071874
5	Aniline	-0.010828	-0.086072
6	N,N-Dimethylaniline	-0.027727	-0.104282
7	p-Toluidine	-0.006652	-0.063327
8	Phenol	-0.127210	-0.190225
9	Benzyl alcohol	-0.060992	-0.063362
10	Anisole	-0.032443	-0.068061
11	Ethoxybenzene	0.141010	0.142533

Trend of Electron-Donating Group Effects on ΔC_0

The substituents was classified into three categories: alkyl groups, amino groups, and oxygen-containing groups (hydroxy and alkoxy) as generally recognized as electron-donating groups (EDGs).However, the computational data presents that the increased electron density from these substituents is not consistently concentrated at the C_0 carbon of the benzene ring. The calculated of C_0 atomic charges tend to become more positive relative to benzene, as shown for alkyl substituents, including toluene, ethylbenzene, isopropylbenzene, and tert-butylbenzene. According to this finding, the inductive electron-donating effect of alkyl groups does not cause an increase in electron density at the carbon atom that is directly connected to the substituent. The delocalized of aromatic π-system is almost caused by the contributed electron density (Imai et al., 2022; Shahamirian et al., 2023). In addition, the observed charge changes are potentially affected by how the electron density is distributed around the C_0 location, which could be induced by the increased steric bulk of larger alkyl substituents.

Resonance donation allows the lone pair electrons on the nitrogen atom to interact with the aromatic π-system in nitrogen-containing substituents such aniline, N,N-dimethylaniline, and p-toluidine (Wieczorkiewicz et al., 2022, 2024). The negative charge at the C_0 location could fail to develop significantly as a consequence of this resonance interaction. As a result, the donated electron density is distributed more evenly over in the aromatic ring, with the para and ortho positions being particularly positions (Stasyuk et al., 2016). Consequently, the change in the C_0 atomic charge remains relatively modest despite the strong resonance-donating capability of amino substituents.

Oxygen-Containing Substituents and Strong Electron Donation

For oxygen-containing substituents including phenol, anisole, and ethoxybenzene, the electric effect is stronger. The oxygen atom in these groups has lone-pair electrons that operate effectively with the aromatic π-system through resonance donation (+R effect). Because of this, oxygen-based substituents tend to donate electrons more strongly than simple alkyl substituents.

In phenol, the hydroxyl group allows it possible for the oxygen lone pair and the aromatic ring to connect strongly through resonance. This interaction makes the spreading of electrons within the π-system stronger, which leads to a clear change in the estimated distribution of atomic charges compared to benzene. Because the hydroxyl group provides both inductive (−I) and

resonance (+R) effects, it changes the total electron density in the aromatic framework in even more ways. (Rusinska-Roszak, 2017).

Another example is alkoxy substituents as ethoxybenzene and anisole, where the oxygen atom contributes electron density to the aromatic ring through resonance. But the electrical equilibrium between resonance and inductive contributions is disturbed when an oxygen-attached alkyl group is present. Through a weak inductive effect, the alkyl group can improve electron donation, and at the same time, it have an impact on the electron density distribution spatially. Hence, compared with hydroxyl substituents, alkoxy substituents typically cause different patterns of charge redistribution (Imai et al., 2022).

Overall, these results indicate that the electronic impact of EDGs on the C_0 atomic charge is governed by a complex interplay between inductive effects, resonance interactions, and substituent structure. Rather than producing a simple localized increase in electron density at C_0, many EDGs redistribute electron density throughout the aromatic π-network. This finding highlights that the electronic response of the C_0 position reflects the global electronic perturbation of the aromatic system rather than a purely local substituent effect.

Role of Inductive and Resonance Effects

The charge distribution at the C_0 carbon is a result of the equilibrium between the substituents' inductive and resonance effects. The primary mechanism by which alkyl groups function is the positive inductive effect (+I), which is achieved by the transfer of electron density due to σ-bonds. Nevertheless, alkyl substituents lack an accumulation of electron density at any one carbon atom in the benzene ring due to its delocalised π-electron system. Rather, it disperses throughout the whole aromatic ring (Comas-Vilà & Salvador, 2025; Sokół et al., 2022).

In contrast, the aromatic π-system capable to interact with the substituents that consist of lone pairs of electrons, such as -NH_2 and -OH, through resonance donation (+R effect). The aromatic framework can be delocalised more effectively, because of this interaction (Wieczorkiewicz et al., 2022). However, a more consistent redistribution of electron density across the ring is another consequence of this delocalisation. Therefore, the inherent electron-donating power of a substituent was not always determined directly by the charge variation at the C_0 location.

Therefore, the ΔC_0 values obtained in this study should be interpreted as indicators of electron redistribution within the aromatic system, rather than as a simple measure of localized charge accumulation at the carbon atom directly bonded to the substituent. This interpretation highlights the importance of considering the combined contributions of inductive and resonance effects when evaluating substituent-induced electronic perturbations in aromatic systems.

Explanation of the Anomalous Behavior of Ethoxybenzene

A fascinating finding in this study reveals that ethoxybenzene's C_0 atomic charge value is not significantly identical as anisole's, even though both molecules have alkoxy substituents. While observing electrons, the –OCH_0 and –OCH_2CH_0 groups have similar source mechanisms that work with the oxygen atom's lone pair electrons. The following allows them interact with the aromatic π-system in a process that is referred to as resonance.

An introduce supplementary inductive contributions and influence the conformational orientation of the substituent relative to the benzene ring resulted a difference observed in ethoxybenzene may be associated with the presence of an additional alkyl chain in the ethoxy substituent Variations in substituent conformation can affect the extent to which the oxygen

lone-pair orbitals overlap with the aromatic π-system, thereby modifying the efficiency of resonance donation. The small variations in molecular geometry lead to noticeable differences in calculated charge distributions at specific atomic positions is detected by semiempirical approaches such as the AM1 method. Consequently, the C_0 charge observed for ethoxybenzene likely reflects a combined effect of oxygen-based resonance donation and additional inductive contributions from the ethyl chain, which together alter the electron density distribution within the aromatic ring.

Consistency Between Löwdin and Mulliken Population Analyses

The Löwdin and Mulliken population analyses differ in magnitude reveal consistent trends in the variation of electron distribution across the examined substituents, although the absolute atomic charge values was obtained. Such differences in absolute charge values are commonly observed between these two population analysis approaches. Compared with the Löwdin, the Mulliken method often produces larger charge magnitudes, largely due to the way electron density is partitioned between atomic orbitals. Despite differences in absolute values, both methods provide the same substituent trend.

Variation of ΔC_0 Atomic Charge Across Substituted Benzene Derivatives

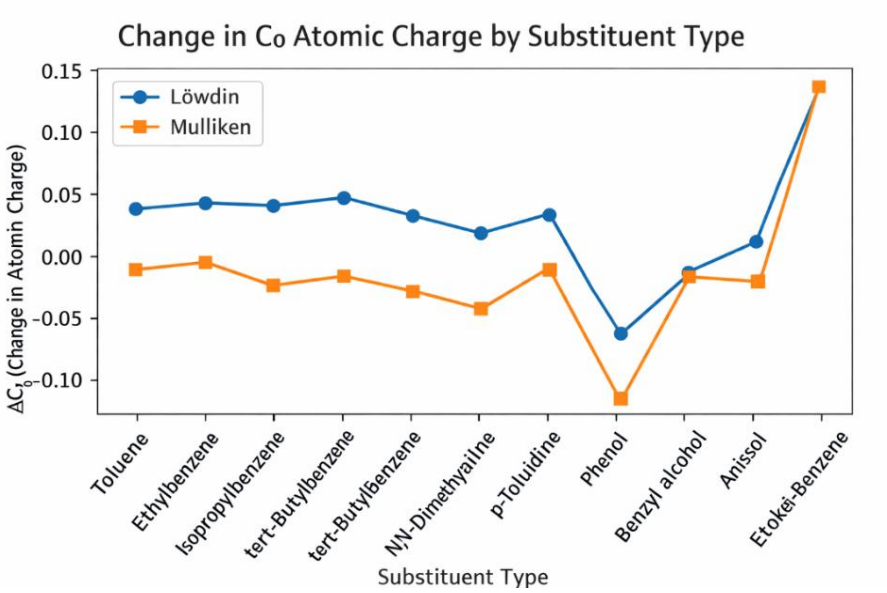

Figure 1. Variation of ΔC_0 Atomic Charge Across Substituted Benzene Derivatives Based on Löwdin and Mulliken Analyses

The graph presents the variation of C_0 atomic charge (ΔC_0) for different electron-donating substituents based on Löwdin and Mulliken analyses. Both methods show consistent trends, although Mulliken values generally have larger magnitudes. Alkyl substituents (toluene, ethylbenzene, isopropylbenzene, and tert-butylbenzene) exhibit only minor changes near zero, indicating that their inductive donation is largely delocalized across the aromatic π-system rather than localized at C_0.

More pronounced effects are observed for heteroatom-containing substituents, particularly oxygen-based groups. Phenol shows the largest decrease in C_0 charge due to strong resonance interaction, while ethoxybenzene displays the highest positive ΔC_0 value as an outlier, reflecting combined resonance and inductive effects. Overall, the results indicate that C_0 charge variations arise from a complex interplay of resonance, induction, and π-electron delocalization rather than simple local electron donation.

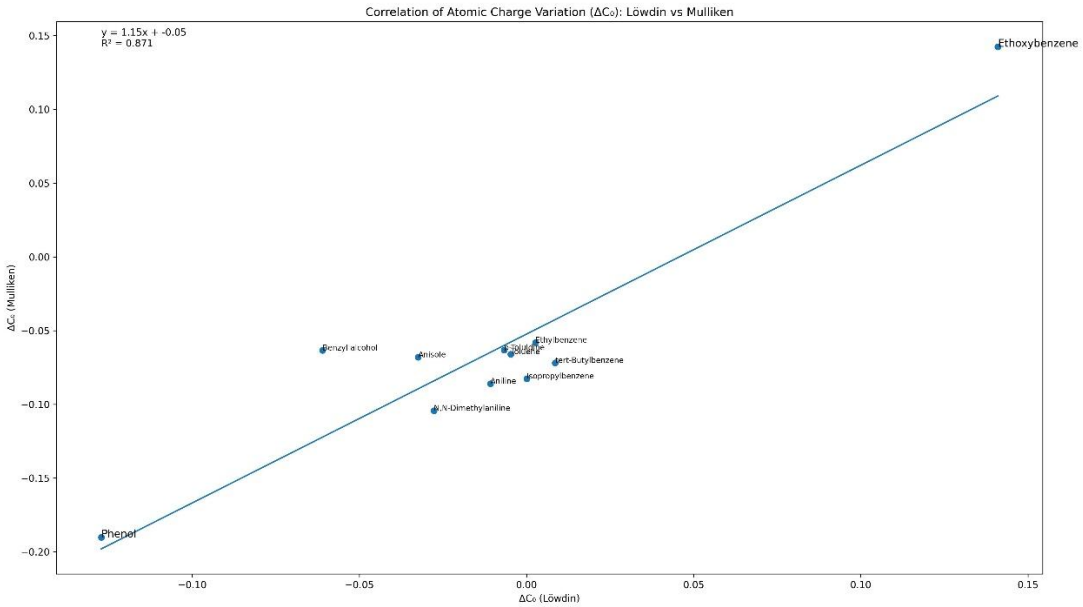

Figure 2. Consistency of ΔC_0 Trends Across Population Analysis Methods

ΔC_0 values from Löwdin and Mulliken analyses show a strong linear agreement, confirming that both methods capture the same underlying electronic effects. The high correlation indicates that the trends arise from intrinsic substituent behavior rather than computational artifacts. While most substituents exhibit similar responses, phenol and ethoxybenzene stand out as clear deviations, reflecting stronger resonance-driven redistribution and combined resonance–inductive effects, respectively. Overall, these results emphasize that substituent effects operate through global electron redistribution rather than localized charge accumulation.

The Average Charge Distribution on C1–C5

The average atomic charge of C1–C5 was calculated to evaluate the overall redistribution of electron density within the aromatic ring after substitution on benzene. Unlike the C_0 carbon, which reflects the local interaction with the substituent, the averaged C1–C5 values provide a broader representation of electron distribution across the remaining π-system of the ring.

Table 2. Average C1–C5 Atomic Charge of Substituted Benzene Derivatives Based on Löwdin and Mulliken Population Analyses

No	Compound	Average C1–C5 Charge (Löwdin)	Average C1–C5 Charge (Mulliken)
1	Toluene	-0.1169652	-0.1683244
2	Ethylbenzene	-0.1183536	-0.1689232
3	Isopropylbenzene	-0.1289562	-0.1879494
4	tert-Butylbenzene	-0.1300920	-0.1887586
5	Aniline	-0.1184886	-0.1634186
6	N,N-Dimethylaniline	-0.1095208	-0.1533404
7	p-Toluidine	-0.1061650	-0.1421128
8	Phenol	-0.0866146	-0.1346210
9	Benzyl alcohol	-0.1253692	-0.1852240
10	Anisole	-0.1092786	-0.1560062
11	Ethoxybenzene	-0.1439628	-0.2026846

For several derivatives such as p-toluidine and N,N-dimethylaniline, the aromatic ring becomes slightly asymmetric due to additional substituent groups, leading to small variations in charge among individual carbon atoms. Averaging the C1–C5 charges therefore allows the electronic effect of substituents to be interpreted at the ring level, reducing the influence of local positional differences. Most substituents produce only minor changes in the average C1–C5 charge relative to benzene. Alkyl substituents (toluene, ethylbenzene, isopropylbenzene, and tert-butylbenzene) exhibit values within a narrow range, indicating that their inductive donation primarily contributes to π-electron delocalization rather than localized charge accumulation within the aromatic ring.

Nitrogen-containing substituents such as aniline, N,N-dimethylaniline, and p-toluidine display a slightly stronger electronic influence due to resonance interaction between the nitrogen lone pair and the aromatic π-system. However, the average C1–C5 charges remain moderate, suggesting that the donated electrons are distributed across the aromatic framework rather than concentrated in specific ring positions.

A more pronounced effect is observed for oxygen-containing substituents. Phenol shows the least negative average C1–C5 value, indicating a relatively higher electron density in the aromatic ring due to strong resonance donation from the oxygen lone pair. In contrast, ethoxybenzene exhibits the most negative average value, suggesting that the electronic distribution is influenced by the combined contribution of oxygen resonance and the inductive effect of the ethyl chain.Overall, the variation in average C1–C5 charges reflects the combined influence of resonance interaction, inductive effects, and π-electron delocalization within the aromatic system rather than a simple localized donor effect.

Average C1–C5 Charge Distribution Reveals Substituent-Dependent Electron Delocalization in Benzene

Electron distribution of substituents, with regards to benzene as the reference system, is illustrated by various patterns in the plot of the average C1-C5 charge. The symmetry of the aromatic π-system in benzene causes its charge distribution to be rather uniform. The electrical distribution across the ring carbons is slightly altered upon substitution, as seen in toluene, aniline, and anisole, but the overall differences remain reasonably close to those of benzene. As a result of the poor effect of alkyl substituents on the redistribution of ring electron density, toluene demonstrates just a small variation. On the other hand, since aniline and anisole contain heteroatoms with lone pairs that can interact with the aromatic π-system, their modifications are more evident. Because of their significantly larger charge changes than the other substituents, phenol and ethoxybenzene become out from the graph too. The electron distribution within the benzene ring is influenced by resonance interaction, inductive effects, and π-electron delocalisation rather than a single electronic effect, as shown by these variations. There seems to be a straightforward linear relationship between the general electron-donating strength of aromatic systems and the substituent-induced electronic changes, according to the trend.

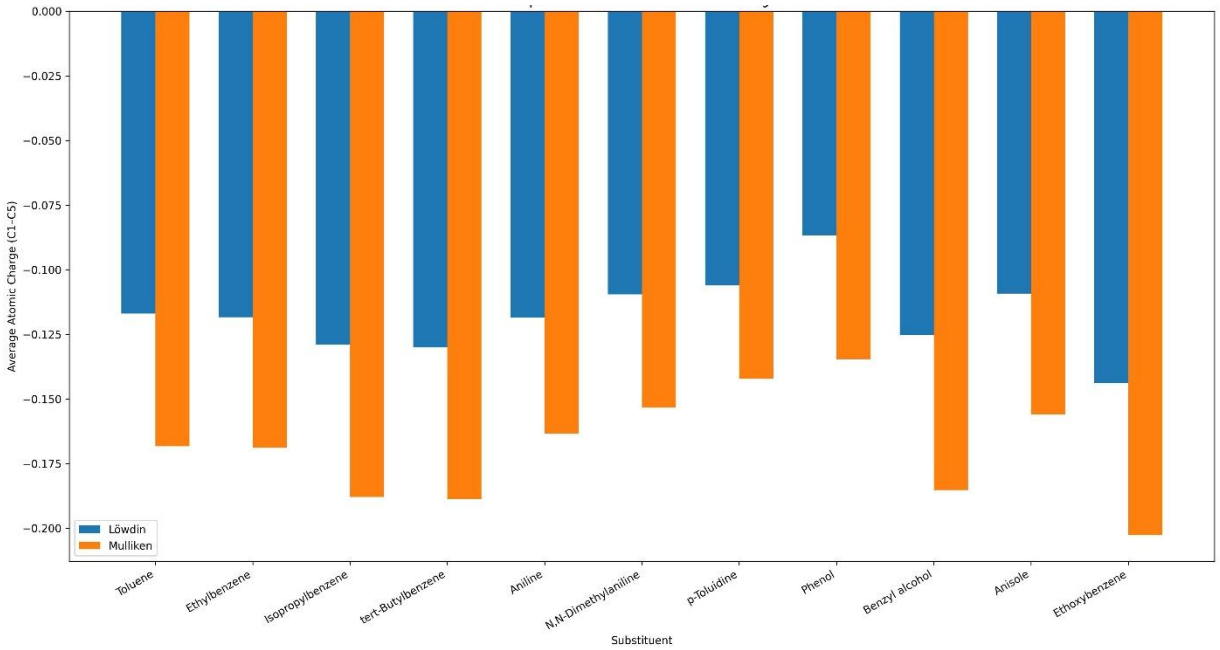

Figure 3. Average C1–C5 Atomic Charge Distribution
in Substituted Benzene Based on Löwdin and Mulliken Analyses

CONCLUSION

This study concludes that the electrical effect of electron-donating substituents on substituted benzene is most effectively interpreted as a worldwide redistribution of electrons in the aromatic π-system, rather than a straightforward local increase in electron density at the C_0. By showing consistent patterns in both the Mulliken and Löwdin population analyses, the computational approach is proven to be innovative and robust, and ΔC_0 is further reinforced as a reliable comparative descriptor. The effects of alkyl and amino substituents are rather small compared to those of oxygen-containing groups, which cause more noticeable electronic perturbations as a result of effective resonance interactions; ethoxybenzene exemplifies this point by showing how structural and inductive factors modify charge distribution. By highlighting that atomic charge changes should be considered as part of a collective electrical response of the aromatic framework rather than as isolated local occurrences, these findings provide a more physically relevant explanation of substituent effects.

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