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Capturing electronic substituent effect with effective atomic orbitals†

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The occupations of the effective atomic orbitals (eff-AOs) of the carbon atoms in the aromatic ring serve as the basis for deriving accurate descriptors of the inductive (F) and resonance (R) effects exerted by substituents in substituted benzene derivatives. The eff-AOs enable a clear separation of the σ-type electron density into contributions originating from the C−H/X bonds (where X represents a substituent) and those from the C−C bonding framework. Our analysis reveals that the inductive effect of a substituent is effectively captured by the shift in the occupation of the eff-AOs associated with the C−C bonding framework at the *meta* position. In contrast, the resonance effect is well-described by the shifts in the occupations of the $2p_z$-type eff-AOs at the *ortho* and *para* positions. The two introduced descriptors for inductive and resonant effects, namely I^X and R^X, are also applied to predict Hammett's σ_m and σ_p in *meta*- and *para*-substituted benzoic acid derivatives. In the case of the *meta*-substituted derivatives, the predictions of the σ_m values are excellent, with a mean average error of just 0.04. This approach provides a robust and systematic framework for quantifying substituent effects in aromatic systems.

Introduction

The substituent effect refers to the influence that a substituent – according to IUPAC,[1] an atom or group of bonded atoms that can be considered to have replaced a hydrogen atom (or two hydrogen atoms in the special case of bivalent groups) in a parent molecular entity (real or hypothetical)-has on the physical and chemical properties of the molecule to which it is attached. The substituent effect can alter the reactivity, stability, and electronic distribution within the molecule, influencing reaction mechanisms, reaction rates, and the outcome of chemical reactions.

One can distinguish different types of substituent effects. Some effects take place through space, like the steric or field effects. In the steric effect, large substituents can cause steric hindrance, affecting the molecule's shape, reactivity, and ability to undergo certain reactions. In the so-called field effects, it is the local electric field created by a substituent can influence the electron distribution in the rest of the molecule.

Hammett parameters, derived from the pioneering work of Hammett in the 1930s, are fundamental tools for understanding and quantifying the through-bond substituent effects. These parameters, expressed as σ values, provide a quantitative

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measure of how substituents influence the electron distribution and chemical reactivity. By correlating the rates or equilibrium constants of reactions with these substituent constants, the Hammett equation[2,3]

$$\log \frac{K_X}{K_H} = \rho \sigma_X \qquad (1)$$

offers a powerful framework for predicting and rationalizing the behavior of organic molecules in various chemical processes. In the original work, Hammett's constants were derived from the ionization constants of substituted benzoic acid. In eqn (1), K_H is the ionization constant for the unsubstituted benzoic acid and K_X is the corresponding constant for *meta*- or *para*-substituted benzoic acid measured in water at 25 °C (*ortho* substitution is not included as it involves steric effects). The reaction constant ρ depends on the type of reaction but not on the substituent used, and for the ionization of benzoic acid is set to 1. Following the free-energy relationships, Hammett's equation can also be applied to the substituent effect on reaction rates.

Hammett parameters are an indispensable tool for mechanistic studies in organic chemistry, particularly valuable for rationalizing reaction mechanisms by providing insights into how electronic effects influence the rate-determining steps and intermediates involved in a chemical reaction. In the original ionization reaction of benzoic acid, electron-withdrawing groups (EWG) accelerate the reaction, because they can stabilize (delocalize) the negative charge that is built in the transition state. Conversely, electron-donating groups (EDGs) destabilize

the transition state, leading to a decrease in the reaction rate. Consequently, EWGs exhibit a positive substituent constant ($\sigma > 0$) while $\sigma < 0$ for EDGs. Different reaction mechanisms exhibit distinct ρ values. For example, a nucleophilic aromatic substitution (SNNAr) mechanism typically shows a large positive ρ value because EWGs stabilize the negatively charged Meisenheimer intermediate. In contrast, an electrophilic aromatic substitution (EAS) mechanism might show a negative ρ value, as electron-donating groups stabilize the positively charged arenium ion intermediate. Hammett plots can thus be used to distinguish between competing mechanisms. Also, a linear correlation suggests a consistent mechanism across different substituents, while deviations from linearity (e.g., in cases of steric effects) can indicate a change in mechanism or the involvement of additional factors.

To achieve a comprehensive understanding and rationalization of the σ values, the electronic effect of substituents has historically been factorized into different contributions. In one of the earlier attempts, Taft decomposed the σ_p and σ_m parameters into field/inductive (σ_F) and resonance (σ_R) contributions as[4–6]

$$\sigma_p = \sigma_F + \sigma_R \quad \text{and} \quad \sigma_m = \sigma_F + \alpha\sigma_R, \tag{2}$$

where α accounts for the fall-off of the resonant effect from *para* to *meta* position. Typical values range from 0.4 down to 0.1 in the case of strong resonant interactions.[4] The field/inductive effect describes electrostatic interactions through space and the intervening sigma bonds, while the resonance or mesomeric effect accounts for the charge transfer to or from the substituent orbitals of suitable symmetry with the π orbitals of the ring and the consequent electron delocalization in conjugated systems. Taft relied on an earlier analysis of the substituent effect by Roberts and Moreland,[7] who used a non-aromatic 4-substituted bicyclo[2.2.2]octane-1-carboxylic acid as a framework, to prevent any resonance contribution. This afforded the σ_F values, which were then used to estimate the corresponding σ_R directly from eqn (2). Alternatively, Charton et al.[6] evaluated σ_F by using the ionization constants of substituted acetic acids as a basis. Later on, Swain and Lupton also considered a similar decomposition of the constants into F (for inductive/field) and R (for resonance) contributions of the form[8]

$$\sigma_p = a{\cdot}F + R \tag{3}$$

The field/inductive term was derived again from the bicycle [2.2.2]octane-1-carboxylic acids constants whereas the resonance term was calculated from eqn (3), assuming that for the $N^+(CH_3)_3$ substituent the R contribution was zero. The adjusted a value was close to unit (0.92), so this approach is not fundamentally different from Taft's given by eqn (2). Inductive/field contributions were also derived from the shift of the shielding of fluorine nuclei in ^{19}F NMR measurements of *meta*-substituted fluorobenzenes.[9,10]

In 1991, Hansch et al.[11] justified that field/inductive parameters could indeed be reliably obtained from different sources, provided the data was carefully treated (for instance, Swain and Lupton's F values were not on the same scale as the

original Hammett's parameters and had to be rescaled[12]). In their seminal review, they compiled a comprehensive collection of σ_p and σ_m constants for more than 500 substituents. They used the simple linear relationship $F = 1.297\sigma_m - 0.385\sigma_p + 0.033$ to derive filed/inductive (F) parameters (also discussing alternative values obtained from several different sources), and from them used the relationship $\sigma_p = \sigma_F + \sigma_R$ to obtain the corresponding reference resonant R (σ_R) parameter values. This contribution still stands as the main source of data of the field.

The resonance/mesomeric contribution, σ_R or R, is more difficult to quantify. In some cases, strongly electron-withdrawing or strongly electron-donating substituents don't fall on the line predicted by the Hammett correlation.[13,14] In fact, while Swain and Lupton claimed that a single R value should describe each substituent, Brown[15,16] and later Hansch[11] advocated for different parametrizations when there is a strong resonance delocalization between the substituent and the reaction center, developing σ_p^+ and σ_p^- constants. These modified Hammett constants in combination with the appropriate F values can be used in eqn (3) to derive the respective R^+ and R^- constants.

Hammett's σ parameters are typically obtained through experimental measurements, but efforts have been made to estimate the values by computational methods, in particular, to find descriptors to account for the field/inductive and resonance effects. The development of new descriptors to predict σ constants is justified by the need to address the limitations of traditional Hammett parameters. Traditional σ values are derived primarily from benzoic acid ionization or similar reactions, which may not fully capture the electronic effects of substituents in more complex or diverse chemical environments. Also, for new or complex substituents, experimental determination of σ values can be time-consuming and resource-intensive.

Theoretical methods have provided insight into the electronic substituent effects by confronting the original Hammett parameters with various descriptors as validation. For example, good correlations have been observed between descriptors derived from the molecular electrostatic potential (MESP) of substituted benzene and Hammett σ values. Field/inductive effects have been related to the critical points (minima) obtained from the topological analysis of the MESP,[17–19] while resonant effects have been rationalized in terms of the difference in the values of the MESP at the *meta* and *para* carbon atoms of substituted benzene derivatives.[20]

Energetic descriptors have also been shown to correlate with σ constants. In particular, the strength of π-conjugation, quantified in the framework of energy decomposition analysis (EDA)[21] by the π-type contribution to the orbital interaction term in *meta*- and *para*-substituted benzylic cations and anions, exhibited surprisingly good correlations with σ_m and σ_p constants,[22] despite inductive effects are in principle ignored with such descriptor. Another energy-based descriptor is the so-called substituent effect stabilization energy (SESE), which uses homodesmotic reactions to quantify the energetics between substituent X and reaction site Y in a given framework R[23,24]

$$SESE = E(R - X) + E(R - Y) - E(X - R - Y) - E(R) \tag{4}$$

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A positive SESE value indicates a favorable substituent effect of X on site Y. Good correlations of the SESE descriptor with σ_m and σ_p constants were found for *para*- and *meta*-substituted fluoro- and trifluoromethylbenzene derivatives.[25,26] Differences in total energies between *para*- and *meta*-substituted benzene derivatives have also been explored by Jabłoński *et al.*[27,28]

Several alternative descriptors are rooted in the changes in the charge distribution upon substitution. For instance, Sadlej-Sosnowska[29–31] introduced the so-called charge of the substituent active region (cSAR), defined as the sum of partial atomic charges at all atoms of the substituent X and the *ipso* carbon atom in monosubstituted benzenes

$$cSAR(X) = q(X) + q(C_{ipso}) \qquad (5)$$

The cSAR values are typically negative for EWGs and positive for EDGs. The authors found a good correlation between cSAR and Hammett's σ constants, independently of the population analysis used.[32] On the other hand, descriptors to account for electron donor–acceptor properties were also introduced in the particular context of the natural population analysis (NPA).[33] The sEDA and pEDA descriptors were introduced to account for the σ and π electron shift induced by the substitution in benzene derivatives.[34] The σ-effect is captured by comparing the sum of the occupancies of the 2s, $2p_x$, and $2p_y$ valence natural atomic orbitals (NAOs) along the six carbon atoms of the substituted benzene and those of benzene. For the π-effect only the occupancies of the $2p_z$ natural atomic orbitals are considered. Unlike the previously mentioned descriptors, the sEDA descriptor correlates with electronegativity scales of substituents (in particular those from Boyd and Boyd-Edgencombe[35,36]), because it contains contributions from the *ipso* carbon (*vide infra*). The pEDA descriptor, however, does exhibit very good correlation with the σ_R parameter, indicating a proper separation of the inductive and resonance effects. A similar strategy has been applied to describe the substituent effect in other molecular frameworks like azoles,[37] heterocycles,[38] double-bonded substituted pi-electron cyclic systems,[39] mono- and disubstituted fulvene derivatives[40,41] and *meta*- and *para*-X-substituted nitrobenzene derivatives.[42]

In this work, we introduce charge-density-based descriptors to properly account for inductive and resonant substituent effects separately, making use of Mayer's effective atomic orbitals (eff-AOs) and their occupations.[43,44] The eff-AOs are the orbitals of the net atomic density and are obtained straightforwardly from the first-order density, using an atom-in-molecule (AIM) model, as described elsewhere.[45] Disregarding the AIM definition and the underlying basis set used in the molecular calculation, one obtains as many significantly occupied eff-AOs as AOs in the classical minimal basis. The formalism can be easily generalized to correlated wavefunctions and also to molecular fragments, leading to the so-called effective fragment orbitals (EFOs).[46] We have recently shown how the EFOs can be applied in a general manner to asses Lewis acid/base character[47] and also to detect and quantify donor/acceptor interactions in transition metal complexes.[48] This prompted us to explore whether descriptors derived from this formalism could be used to quantify inductive/field and resonance effects.

For this purpose, in this work we considered a large set of mono-substituted benzene derivatives, from which descriptors accounting for field/inductive and resonance effects are proposed, supported by excellent correlations with the available σ_F (F) and σ_R (R) parameters. In addition, descriptors related directly with Hammett's σ_m and σ_p parameters were obtained considering the corresponding *meta*- and *para*-substituted benzoic acid derivatives.
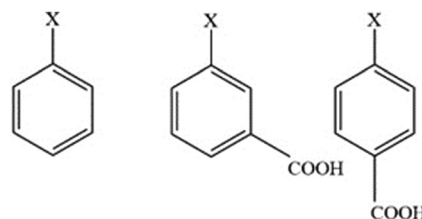
Computational details

All DFT calculations were carried out with Gaussian16.[49] All geometry optimizations were performed using the BP86 density-functional[50,51] coupled with the def2TZVP basis set.[52] The spin-resolved EFOs have been obtained with the APOST-3D program.[53] The topological fuzzy Voronoi cells (TFVC)[54] atomic definition, a fuzzy-atom efficient and robust real-space alternative to QTAIM, has been used.

All the substituent constants used in this work and listed in the ESI† are the F and R modified Swain–Lupton parameters and the Hammett constants tabulated in the review of Hansch *et al.*[11] We chose as model rings a series of mono-substituted benzenes and *meta*- and *para*-substituted benzoic acid. We have considered 33 different substituents spanning a wide range on both σ and π donor–acceptor properties, depicted in Scheme 1. Indeed, according to the experimentally derived tabulated values, they cover the range from strong π-donating, *e.g.* NMe$_2$ and OCH(CH$_3$)$_2$, with $R = -0.98$ and $R = -0.79$, respectively, to π-electron withdrawing groups like COCH$_3$ ($R = +0.17$) or CN ($R = +0.15$).

Results and discussion

Let us start by considering a diverse set of mono-substituted benzene derivatives. All the systems analyzed have a singlet ground state described by a closed-shell Slater determinant within KS-DFT formalism. This means that the eff-AOs (and their occupations) derived from the alpha and beta spin channels are exactly the same. Henceforth, we refer to eff-AO occupations as the sum of the alpha and beta contributions.

X = I, Br, SH, Cl, SiH$_3$, CF$_3$, COOH, COOCH$_3$, CN, H, COCH$_3$, COH, NO$_2$, CHCH$_2$, C$_6$H$_5$, CH$_3$, CH$_2$CH$_3$, NHCOCH$_3$, N(CH$_3$)$_2$, NH$_2$, F, OH, OCH$_3$, SCH$_3$, N(CH$_2$CH$_3$)$_2$, OCH(CH$_3$)$_2$, C$_6$F$_5$, OCH$_2$CH$_2$CH$_3$, Sn(CH$_3$)$_3$, C(CF$_3$)$_3$, OC$_6$H$_5$, COCl

Scheme 1 Set of studied mono-substituted benzene and *meta*- and *para*-substituted benzoic acid derivatives.
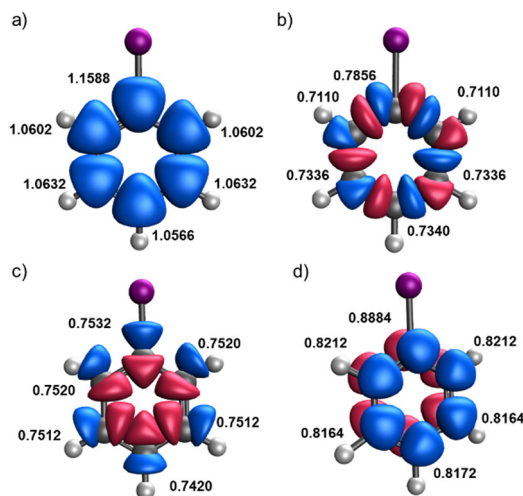
Fig. 1 Overlay of carbon's 2s (a), $2p_{C-C}$ (b), $2p_{C-H/X}$ (c) and $2p_z$ (d) eff-AO shapes and occupation (alpha plus beta) in the monosubstituted iodo-benzene compound.

Our focus is on the electron density changes induced in the ring by the substituent. For this reason, we consider solely the eff-AOs of the carbon atoms of the ring. For illustrative purposes, Fig. 1 shows an overlay of the relevant eff-AOs of all carbon atoms for iodobenzene (C_6H_5I). Each carbon atom exhibits five significantly occupied eff-AOS, in line with the concept of minimal basis. There is a core 1s-type eff-AOs with an occupation very close to 2.0 and the remaining eff-AOs are those depicted in Fig. 1. One can easily identify a slightly polarized 2s-type and different 2p-type eff-AOs one each carbon center. Within the latter, one can recognize in-plane 2p-type eff-AOs (Fig. 1(b)) that are involved in the C–C σ-interactions along the ring, clearly separated from other 2p-type eff-AOs (Fig. 1(c)) that reveal the σ polarization along the C–H and C–X bonds. Finally, one can also identify out-of-plane $2p_z$ –type eff-AOs (Fig. 1(d)), which account for the π-type density distribution along the ring. This represents a fundamental difference with the NAO approach, where $2p_x$ and $2p_y$ AOs with mixed contributions to the C–C and C–H/C–X σ bonding are obtained. Also, contrary to the eff-AOs, a separate out-of-plane $2p_z$ NAO is obtained only if the molecule is placed in the xy plane. Thus, the separation between σ-type and π-type populations is compromised for non-perfectly planar systems.

Fig. 1 reveals a distinct behavior in the occupation numbers of the *ipso* carbon compared to the other carbon atoms in the ring. However, some eff-AOs, such as the 2s and $2p_{C-H/X}$ ones, show only minor variations depending on the carbon atom's position in the ring. In this particular example, the occupation numbers of the *ipso* carbon are not too different from those of the other carbons, as the electronegativities of carbon and iodine are similar. Nonetheless, with most of the studied substituents, these differences are much more pronounced.

The eff-AO occupations that are more sensitive to the carbon position in the ring are the $2p_{C-C}$ and the $2p_z$ ones, and the former should more selectively account for the inductive effect.

The correlation of the $2p_{C-C}$ eff-AO occupation of each carbon atom position with the available F parameters from Hansch *et al.*[11] for the whole set of mono-substituted benzene derivatives can be found in Fig. S1 of the ESI.† Interestingly, the occupations at the *meta* position exhibit a very good correlation with the F parameter ($r^2 = 0.89$), while the correlation is inexistent for all other carbon positions (r^2 values below 0.08). Also, the negative value of the slope indicates that the larger the inductive effect of the substituent, the smaller the occupation of the $2p_{C-C}$ eff-AO in *meta* position. That is, the substituent effectively drains density from the C–C σ bonds involving the carbon in *meta* position.

In the spirit of the Hammett parameters, we introduce a new descriptor, I^X, for the field/inductive effect as the difference of the $2p_{C-C}$ eff-AO occupations in *meta* position (average of the two) of the unsubstituted molecule (*i.e.* benzene) and those of the mono-substituted derivative as

$$I^X = \lambda^{2pC-C}_{(meta,R=H)} - \lambda^{2pC-C}_{(meta,R=X)}. \tag{6}$$

By formulating it as an occupation difference, the descriptor gains greater robustness with respect to the theoretical level used (using real-space methods basis set dependence is virtually eliminated).

We also explored the role of the occupations of the other carbon positions using multilinear regression, but the fitting didn't improve significantly. These findings are in line with previous observations that the field/inductive effect is more pronounced in *meta* position.[37,55,56] They also show that while eff-AO occupations (and overall partial atomic charge) of the *ipso* carbon are the ones that are most affected by the substituent, they do not explain the inductive effect on the ring. At this point, it is worth comparing our I^X index with the aforementioned sEDA descriptor. Both are defined as differences in atomic orbital populations between the unsubstituted and substituted species. In sEDA, the contributions of the valence NAOs of all carbon atoms of the ring are considered, while in I^X we only use one particular eff-AO of one particular carbon position (*meta*). Since sEDA includes the contributions from the *ipso* carbon, which is expected to be dominant, it better accounts for the substituent's electronegativity, as shown by the authors, rather than the inductive effect on the ring. We can readily confirm this hypothesis by considering the most appropriate eff-AO for this purpose, namely the occupation of the $2p_{C-H/X}$ eff-AO of the *ipso* carbon (see Fig. 1(b)). Fig. S2 and Table S1 of the ESI† show an excellent correlation ($r^2 = 0.92$) with the Boyd group electronegativity. In fact, an even better correlation ($r^2 = 0.97$) is found using the occupations of the σ-type eff-AO of the substituent, which is complementary to the $2p_{C-H/X}$ eff-AO of the *ipso* carbon. In recent work,[48] we have used this occupation as a measure of σ-donation of ligands, which is revealed here as closely related to the group's electronegativity scale.

There has been a long debate in the literature about whether the field/inductive effect F is transmitted through space (field) or through bonds (inductive). The early calculations and models suggested that the field effect was predominant,[57–59]

while others advocate for a major role of through-bond transmission.[60–62] A more recent study using density-based descriptors (cSAR) revealed a dominant inductive contribution.[42] However, quantification of both effects with topological analysis of the electrostatic potential seems to indicate that the ratio of through-space/bonds depends on the nature of the substituent.[63] Our present study is not designed to disentangle both effects, but by decomposing the atomic populations in the different eff-AO contributions we identified a unique descriptor that explains the trends in the F parameter and is independent of the electronic structure around the *ipso* or the *ortho* carbon in the ring. This observation can only be explained in terms of a through-bond transmission, indicating an inductive effect.

The plot of the reference F values against the I^X descriptor is shown in Fig. 2. The relationship obtained from the least-squares fit is

$$F = 57.56I^X + 0.043 \qquad (7)$$

The I^X values obtained for the whole set of substituents are listed in Table 1. A first observation is that the nature of the contact atom of the substituent is an important factor for the I^X value, but it is the overall electronic structure of the substituent that ultimately determines the inductive effect. While for X = CH$_3$ or X = CH$_2$CH$_3$ the I^X values are very close to zero, X = C(CF$_3$)$_3$ or X = COCl rank among the highest values of I^X among the set.

In some cases, the same F parameter is tabulated for chemically similar substituents. For example, $F = 0.33$ for both X = COH and X = COCH$_3$, and $F = 0.34$ for both X = COOH and X = COOCH$_3$. However, the I^X descriptor can capture the subtle effect of the methyl substitution. As shown in Table 1, there is a slight but meaningful decrease in the I^X value for the methylated substituents.

Our results also reveal some rather unexpected reference F data. In the series X = OH, OCH$_3$, OCH$_2$CH$_2$CH$_3$ our calculated I^X values show a systematic trend, decreasing from 0.0050 to 0.0046 and 0.0037, respectively, showing again that replacing

Table 1 Field/inductive (F) and resonance (R) parameters from Hansch et al.[11] and calculated I^X and R^X descriptors from the set of monosubstituted benzene derivatives. The correlations obtained are $F = 57.56I^X + 0.043$ ($r^2 = 0.890$) and $R = 14.27R^X - 0.125$ ($r^2 = 0.899$)

Substituent (X)	F (ref. 11)	I^X	R (ref. 11)	R^X
Sn(CH$_3$)$_3$	0.03	−0.0019	−0.03	−0.0024
H	0.00	0.0000	0.00	0.0000
SiH$_3$	0.06	0.0008	0.04	0.0039
CH$_3$	0.01	−0.0010	−0.18	−0.0106
CH$_2$CH$_3$	0.00	−0.0010	−0.15	−0.0084
CHCH$_2$	0.13	0.0008	−0.17	−0.0017
C$_6$H$_5$	0.12	0.0010	−0.13	−0.0027
C$_6$F$_5$	0.27	0.0044	0.00	0.0070
NH$_2$	0.08	0.0020	−0.74	−0.0412
NHCH$_3$	0.03	0.0022	−0.73	−0.0448
NMe$_2$	0.15	0.0024	−0.98	−0.0431
NEt$_2$	0.01	0.0020	−0.73	−0.0432
NHCOCH$_3$	0.31	0.0043	−0.31	−0.0164
SH	0.30	0.0046	−0.15	−0.0177
SCH$_3$	0.23	0.0035	−0.23	−0.0193
COOCH$_3$	0.34	0.0039	0.11	0.0197
COCH$_3$	0.33	0.0042	0.17	0.0190
COOH	0.34	0.0054	0.11	0.0217
COH	0.33	0.0055	0.09	0.0219
OH	0.33	0.0050	−0.70	−0.0338
OCH$_3$	0.29	0.0046	−0.56	−0.0316
OCH(CH$_3$)$_2$	0.34	0.0039	−0.79	−0.0307
OCH$_2$CH$_2$CH$_3$	0.26	0.0037	−0.51	−0.0301
OC$_6$H$_5$	0.37	0.0047	−0.40	−0.0176
F	0.45	0.0080	−0.39	−0.0173
Cl	0.42	0.0056	−0.19	−0.0041
Br	0.45	0.0060	−0.22	−0.0016
I	0.42	0.0060	−0.24	−0.0007
CN	0.51	0.0064	0.15	0.0147
CF$_3$	0.38	0.0066	0.16	0.0125
C(CF$_3$)$_3$	0.53	0.0076	0.02	0.0146
COCl	0.46	0.0081	0.15	0.0281
NO$_2$	0.65	0.0110	0.13	0.0253

hydrogen by alkyl groups in the substituent leads to a decrease in the inductive effect. In this case, this trend is captured also by the reference F values, decreasing from 0.33 to 0.29 and 0.26. However, for X = OCH(CH$_3$)$_2$ the I^X value (0.0039) is close to that of X = OCH$_2$CH$_2$CH$_3$, while the reference F value is 0.34, even higher than that of the strongest substituent of the series, X = OH. This deviation suggests an anomaly in the reference F data for X = OCH(CH$_3$)$_2$.

The largest discrepancies between the reference F and our calculated I^X descriptor are observed for X = NHCH$_3$ and NEt$_2$ substituents. Indeed, by removing these points from the data set the correlation improves significantly to $r^2 = 0.93$. We obtain similar I^X values for X = NMe$_2$ (0.0024) and X = NEt$_2$ (0.0020), as could be expected, but the tabulated F values are 0.15 and 0.01, respectively. Similarly, in the X = NH$_2$, NHCH$_3$, N(CH$_3$)$_2$ series, while we observe a slight but monotonic increase of the I^X values upon methylation, the tabulated F values are 0.08, 0.03 and 0.15, respectively. Again, the F value for the X = NHCH$_3$ is rather unexpected and does not seem to follow a well-defined trend. It is important to recall that the reference F values from Hansch et al.[11] are obtained from the experimentally derived σ_m and σ_p Hammett's constants as assuming a common linear relationship. Our results suggest that the I^X descriptor may provide a more consistent and reliable measure for certain
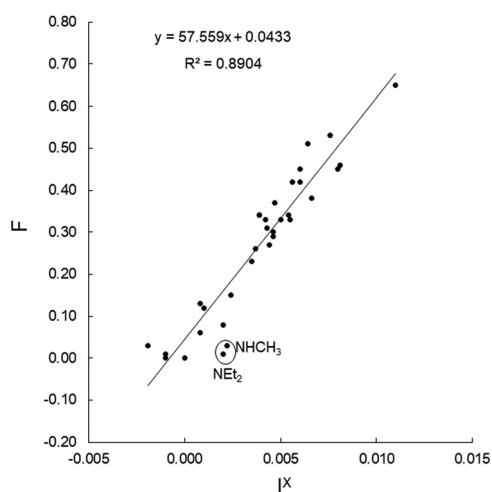

Fig. 2 Experimentally derived F values from Hansch et al.[11] vs. calculated I^X descriptor for the set of monosubstituted benzene derivatives.

substituents, especially in cases where the reference F values might be intrinsically unreliable or deviating from expected trends.

On the other hand, the resonant effect involves electron delocalization through the π system. We repeated the same analysis as for the field/inductive effect and checked the correlation of the occupation of the $2p_z$-type eff-AOs of the different carbon positions on the ring with the reference R parameter from Hansch et al.[11] for the set of monosubstituted benzene derivatives. The results are collected in Fig. S4 of the ESI.† Contrary to the inductive effect, we observe some correlation of the R values with the eff-AO occupation of the *ipso* carbon ($r^2 = 0.600$), and very poor correlation at the *meta* position ($r^2 = 0.315$). It is well-known the fact that EDGs activate *ortho* and *para* positions of the ring.[37,55,56] It is not too surprising that we obtain very good correlation ($r^2 \sim 0.9$) with the eff-AO occupations on either of these positions. Again, a negative slope of the correlation indicates that the larger the resonant effect (+M; $R < 0$), the higher the occupation of the $2p_z$ eff-AO. To match with the original R scale, we define our new descriptor for resonant effect as (the negative of) the sum of the average of *ortho* and *para* $2p_z$ eff-AO occupations in the ring, relative to their value for the unsubstituted system (benzene)

$$R^X = \lambda^{2p_z}_{(o+p,R=H)} - \lambda^{2p_z}_{(o+p,R=X)} \qquad (8)$$

The values obtained for the R^X descriptor are gathered in Table 1. Most of the substituents considered in this work (21) are considered π electron-donating substituents, and 12 out of 33 are π electron-withdrawing. In all cases, the reference R values and R^X have the same sign, namely negative for EDGs and positive for EWGs. Within the former group, one can find the substituents possessing lone pairs such as amines, alcohols, and halides. For all these systems, the $2p_z$ eff-AO occupations in the *ortho*- and *para*-positions are greater than the for the *meta* positions, in line with the *ortho*–*para* activating nature for EAS reactions. However, when we consider EWGs the effect is the opposite. The $2p_z$ EFOs occupations in *meta* position are (slightly) higher than in the *ortho* and *para* carbon centers, again explaining the observed regioselectivity of EAS reactions.[64]

Fig. 3 (left) shows the correlation of our R^X descriptor with the R parameter from Hansch et al.[11] The relationship obtained through the fitting is

$$R = 14.27R^X - 0.125 \ (r^2 = 0.899) \qquad (9)$$

The r^2 value is similar to that obtained for the F parameter, but the y-intercept shows a more marked deviation from the ideal zero value. This somewhat less satisfactory behavior could be expected, as the range of values of R is much wider than for F. The main outliers of the correlation are X = SH ($R = -0.15$) and X = N(CH$_3$)^2 ($R = -0.98$). The deviation for X = OCH(CH$_3$)$_2$ ($R = -0.79$) is also large, but the experimentally derived R-value is suspected of being accurate, as the authors noticed in their review.[11]

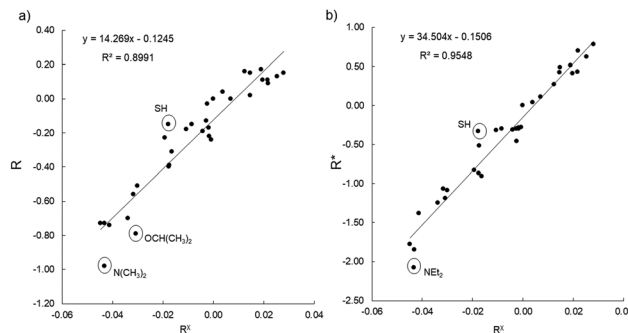Although the monosubstituted benzene derivatives considered here are not charged, it appears that the R^X descriptor

Fig. 3 Experimentally derived R values (left) and R^* (right, see text) from Hansch et al.[11] vs. calculated R^X descriptor for the set of monosubstituted benzene derivatives.

provides a better description of the modified R^+ and R^- substituent constants for EWGs and EWGs, respectively. In Fig. 3 (right) we plot the R^X values against the R^* constants, where R^* represents R^+ for EWGs and R^- for EDGs. The range of R^* values is significantly wider compared to the original R parameters. The correlation is excellent ($r^2 = 0.95$), although the y-intercept still shows slight deviations from the ideal zero value. The ratio of the slopes of the correlations (*ca.* 2.4) is not far from the enhancement ratio of *ca.* 1.9 described by Hansch et al.[11] for the R^+ and R^- values relative to R. In the case of X = SH, the reference R^- value is still somewhat too low compared to our prediction. The calculated R^X values for X = NMe$_2$ (-0.431) and X = NEt$_2$ (-0.432) are very similar. However, the latter appears to be an outlier, because the reference R^- value of -2.08, is much lower than for the chemically similar X = NMe$_2$ ($R^- = -1.85$). This discrepancy, however, is due to the abovementioned unexpectedly different reference F values.

To further test the predictive power of the descriptors derived from the occupations of the eff-AOs, we have also studied *meta*- and *para*-substituted benzoic acid derivatives using the same set of 33 substituents. The goal is to test the ability to predict directly the respective Hammett's σ_m and σ_p constants. We have obtained the eff-AOs and their occupations for all carbon atoms of the ring in the set of *meta*- and *para*-substituted benzoic acid derivatives. The results can be found in the ESI.†

The *meta*-substituted derivatives have two distinct *meta* positions relative to the substituent X: the one also in *meta* relative to the carboxylic group and the *ipso* carbon relative to the carboxylic group. We have observed that the variations of the $2p_{C-C}$ eff-AO occupations of the former are very similar to those observed for the monosubstituted benzene derivatives. Indeed, the values of the I^X descriptor using only this *meta* position in the *meta*-substituted benzoic acids correlate very well ($r^2 = 0.92$, see Fig. S5, ESI†) with the I^X values obtained for mono-substituted derivatives using eqn (6). However, the correlation is much worse if including also the contributions from the *ipso* carbon.

This is not the case of the R^X descriptor, where the individual contributions from the *ortho* and *para* positions relative to X exhibit a very good correlation between them ($r^2 = 0.91$).

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In fact, the overall R^X values obtained are in almost perfect agreement with those obtained for the mono-substituted benzene derivatives (see Fig. S6, ESI†). Such an excellent transferability of the resonant effect can be ascribed to the fact in the *meta*-substituted benzoic acid derivatives, the *ortho* and *para* positions with respect to substituent X are also in *ortho* and *para* with respect to the carboxylic group.

Once we have established that the I^X (excluding the *ipso* carbon) and R^X indices derived from the *meta*-substituted benzoic acid derivatives are proper descriptors for the inductive and resonant effects, respectively, we can attempt the quantification of both effects in the value of Hammett's σ_m parameter. The correlation of I^X against the experimental σ_m values is significant ($r^2 = 0.77$), but cannot fully explain the trends. Considering also the R^X descriptor in a multilinear fit yields the following relationship

$$\sigma_m = 53.58 I^X + 5.12 R^X + 0.053 \quad (r^2 = 0.950) \quad (10)$$

The mean unsigned error in the σ_m values using eqn (10) is just 0.04, incidentally roughly the same uncertainty associated to the expression used by Hansch *et al.*[11] to derive the F parameter from experimental σ_m and σ_p values. The worst prediction is for X = SH (0.09 calculated *vs.* 0.25 experimental), a substituent that already showed significant deviations in the resonant effect.

The slopes of the I^X and R^X terms in eqn (10) seem to indicate a much larger contribution to the σ_m value from the former. However, the slopes are misleading because the range of values of the R^X parameter is much larger than for the I^X one. This is because the σ framework is much more rigid than the delocalized π system, so the shift in the σ-type eff-AO populations is much smaller. But, combining eqn (7) and (9) with eqn (10) we find an expression of the σ_m values in terms of the modified Swain and Lupton F and R parameters:

$$\sigma_m = 0.928 F + 0.259 R + 0.054. \quad (11)$$

We can see that indeed the field/inductive contribution is dominant in σ_m, with a coefficient close to 1, consistent with the relationship described in eqn (2). Also, the coefficients for R (0.359) is very close to the original 1/3 value introduced by Taft.[4]

On the other hand, it is worth mentioning that the I^X values obtained including also the contribution of the *ipso* carbon show a much better correlation with the experimental σ_m values ($r^2 = 0.878$, see Fig. S7, ESI†). This relationship is not as good as the one described by eqn (10), but highlights the classical view that the σ_m values can to a large extent be explained in terms of field/inductive effects.

Analyzing *para*-substituted benzoic acid derivatives is inherently more complex than their *meta*-substituted counterparts. This is because the carbon positions that are *meta* to the X substituent are *ortho* to the carboxylic group, and *vice versa*. Furthermore, the *para* position relative to one substituent corresponds to the *ipso* position relative to the other. Since both substituents simultaneously exert inductive and resonant effects, their combined influence creates a more intricate

interplay, making it difficult to disentangle their individual contributions.

As a result, the changes in the occupations of the $2p_{C–C}$ eff-AOs at the *meta* position relative to substituent X do not correlate as well with the F parameter as they do in mono-substituted benzene derivatives. This is reflected in the poor correlation ($r^2 = 0.61$) between the I^X parameter calculated for *para*-substituted derivatives and the reference F values. In contrast, the shifts in the $2p_z$ eff-AO occupations at both *ortho* and *para* positions are similar to those observed in mono-substituted benzene derivatives. This similarity allows the R^X descriptor, calculated for *para*-substituted derivatives, to perform equally well, showing a strong correlation ($r^2 = 0.90$) with the R parameter. The correlation further improves ($r^2 = 0.96$) when using the set of R^* parameters, partly due to the broader range of R^* values. However, as previously noted, the X = SH and X = NEt$_2$ substituents remain outliers, exhibiting significant deviations from the general trend.

In the tables provided by Hansch *et al.*,[11] the σ_p values are precisely broken down into contributions from F (field/inductive) and R (resonance) effects. However, it is the R contributions that play a more significant role in determining the σ_p values, ultimately defining whether the substituent is classified as EDG or EWG in nature. Hence, the correlation between the σ_p values and solely the R^X descriptor calculated for the *para*-substituted benzoic acid derivatives is quite good, too ($r^2 = 0.88$, see Fig. S8, ESI†). To unveil the role of the field/inductive term we have performed a multilinear regression including also the I^X descriptor, leading to the relationship

$$\sigma_p = 10.17 I^X + 63.36 R^X + 0.018 \quad (r^2 = 0.926) \quad (12)$$

The correlation improves and the r^2 value is not too different from eqn (10) for the σ_m values, but the mean average error is twice as large (0.085). We have observed that a better fit ($r^2 = 0.95$, MAE = 0.075) is obtained by including in the I^X calculation also the $2p_{C–C}$ eff-AO contributions in *ortho* positions with respect to the X substituent. The rationale is that these positions are also in *meta* with respect to the carboxylic group.

Conclusions

In this study, we have developed a robust and systematic framework for quantifying substituent effects in aromatic systems by leveraging the occupations of the eff-AOs of the carbon atoms in the benzene ring. The key advantage of the eff-AOs lies in their ability to extract the σ-type contributions to the electron density from the C–C bonding framework in the ring. We show that the inductive effect of a substituent is effectively captured by the shift in the occupation of the eff-AOs associated with the C–C bonding framework solely at the *meta* position. Conversely, the resonance effect is well-captured by the shifts in the occupations of the $2p_z$-type eff-AOs of the carbon atoms at the *ortho* and *para* positions. The introduced descriptors, I^X and R^X, for inductive and resonance effects, respectively, display

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excellent correlation against the modified Swain and Lupton F and R (or R^+/R^-) parameters compiled by Hansch *et al.*[11] for a chemically diverse set of 33 substituents. Our descriptors do not align well with certain F and R reference values, particularly for X = SH and specific amino-type substituents. While the origin of these discrepancies remains unclear, it raises the possibility that some reference values may warrant re-evaluation or could be influenced by experimental or methodological inconsistencies

The I^X and R^X descriptors were also applied to predict Hammett's σ_m and σ_p constants, considering explicitly *meta*- and *para*-substituted benzoic acid derivatives. In the *meta*-substituted derivatives, the transferability of both descriptors for inductive and resonance effects obtained with the mono-substituted benzene derivatives was excellent. This leads to very accurate predictions of the σ_m values, with a mean error of just 0.04 units across the set of substituents. The prediction of experimental Hammet's σ_p values proved to be more challenging, with average errors around 0.08 units.

Overall, this work establishes a clear connection between the electronic structure of aromatic systems and the empirical Hammett parameters, paving the way for more accurate and interpretable models in physical organic chemistry. Our approach not only provides a deeper understanding of the electronic interactions in substituted benzene derivatives but also offers a practical tool for predicting substituent effects in aromatic systems.

Author contributions

G. Comas-Vilà (investigation, data curation, methodology, writing – original draft). P. Salvador (conceptualization, resources, methodology, software, supervision, writing).

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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