Theoretical Calculation of Ionization Potentials for Disubstituted Benzenes: Additivity vs Non-Additivity of Substituent Effects

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The ionization potentials of 55 para- and 55 meta-disubstituted benzenes, consisting of all binary combinations of electron-withdrawing groups ($-NO_2$, $-CF_3$, $-CHO$, $-COOH$) and electron-donating groups ($-Cl$, $-CH_3$, $-OH$, $-OCH_3$, $-NH_2$, and $-N(CH_3)_2$) have been calculated using density functional theory with the B3LYP functional and a 6-31G(d) basis set. Relative ionization potentials (ΔIP), referred to benzene, are compared with experimental values and shown to be in good agreement. The disubstituted data were correlated with monosubstituted ΔIP data and shown to require quadratic terms in order to achieve a good fit; the validity of this conclusion was possible due to the low scatter in the calculated data. A simple MO analysis gives a semiquantitative interpretation of the observed trends in substitutent effects, including a discussion of combinations of substituents for which nonadditivity should be expected.

Introduction

The study of substituent effects on properties of benzene has a venerable history perhaps dating back to the early 1960s, following the seminal work of Hammett.[1] Early reviews by Topsom et al.[2] discussed the significance of substituent effects and gave a qualititative interpretation in terms of resonance and inductive effects. A firm MO basis for the discussion was provided by the perturbation molecular orbital (PMO) theory of conjugated systems.[3] This was developed and applied more fully to the case of benzene with several substituents by Pross and Radom,[4] which drew on earlier work of Hehre et al.[5] on monosubstututed benzene. These concepts are now well accepted in the literature[6] and are applied regularly in the discussion of properties such as bond dissociation enthalpies.[7]

Despite the huge volume of work published on substituent effects, very few studies have appeared where substituent effects on the ionization potential of substituted benzenes are examined. The most thorough work in this area was reported by Crable and Kearns,[8] who made reliable quantitative measurements of mono- and disubstituted benzenes. These authors also reported the correlation of IPs with σ^+ values[1] and reported linear correlations for substituted benzenes and substituted toluenes. Later studies by Johnstone et al.[9] extended the work of Crable and Kearns and introduced into the literature a σ_{IP} scale based on vertical ionization potentials.

At the present time, a number of developments in density functional theory (DFT) have led to significant improvements in the ability to calculate gas-phase ionization potentials, so that detailed comparisons with experimental data have become meaningful. For example, De Proft and Geerlings[10] did a systematic study of small molecules using various DFT methods and the G2 thermochemical data set.[11] They found that both the B3LYP and the B3PW91 functionals gave mean absolute deviations of 0.15 eV (3.5 kcal/mol) for basis sets of spdf quality. However, studies on larger systems including disubstituted benzenes seem to be quite limited. Fox and Kollman (FK),[12] in their study of substituted benzenes, noted that they could find no previous ab initio or density functional theory studies of the ionization potentials of these systems. In their study, FK found that the B3LYP density functional was optimum, but use of a 6-31G(d) basis set led to a systematic error of about 10 kcal/mol, the calculated values being generally too low. Their data for *p*-nitrotoluene, however, seemed anomalous compared to their other results.

A number of other DFT studies have examined substituted ethylenes[13a] or more complex aromatics[13b] and generally agree that the B3LYP functional is best suited to IP studies, usually being superior to ab initio methods such as MP2 that often show serious spin contamination in the cation.[12] Our own work on mono- and polysubstituted benzenes[14] showed that by obtaining geometries and frequencies at the AM1 level,[15] followed by a B3LYP[16]

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single-point energy calculation, we could obtain IPs for monosubstituted benzenes that differed systematically from experiment by ca. 10 kcal/mol for a 6-31G(d) basis set, or 5 kcal/mol using a 6-311G(d) basis set. However, no improvement in correlation coefficient was noted on going to the larger basis set, and thus, these systematic errors could easily be corrected for by simply referring IP values to a suitable reference calculated with the same basis set. When that is done we obtain ΔIP values, where $\Delta IP = IP$ (benzene reference) $- IP$ (substituted benzene), and these ΔIP values will be shown to correlate very well with experimental data, also taken as ΔIPs.

Another motivation for the present paper is the desire to predict accurate IPs in a variety of substituted benzenes and related systems, to help determine reaction mechanisms in systems that could deactivate free radicals by either hydrogen transfer or electron transfer. The former requires an accurate treatment of the bond dissociation enthalpy (BDE), e.g., as in $RO_2^{\bullet} + ArO-H \rightarrow ROOH + ArO^{\bullet}$, since the reaction rate is determined by the BDE of the OH bond in the parent phenol. For example, FK looked at enzyme-catalyzed reactions[12] and tried to determine by calculating both gas-phase BDE and IP data whether the mechanism occurred by an H-atom or electron-transfer process. Recently, we presented a new methodology for accurate calculation of O−H BDE's in phenols,[17a] which was then further improved for treatment of X−H bonds[7a] or carbon−halogen bonds.[17b] Deactivation by electron transfer, on the other hand, corresponds to the multistep mechanism in which the first step is $RO_2^{\bullet} + ArH \rightarrow ROO^- + ArH^+$, i.e., with formation of the radical cation ArH^+. The rate of this process will depend on the IP of the parent ArH, thus requiring an accurate calculation of this quantity as well as the BDE. We considered this type of calculation in our first paper on IPs,[14] where we concentrated on the calculation of monosubstituted benzene.

The relevant questions we address in this paper are the following: Given a wide range of electron-withdrawing and electron-donating substituents, do the calculated ΔIP data for disubstituted benzenes agree well with the experimental data? If so, under what conditions will the individual substituent effects for the two substituents be additive? Finally, is there a simple MO interpretation, e.g., a PMO analysis, which can explain all the trends in the disubstituted benzene data? As will be seen, we are able to provide some definitive answers to these questions and provide empirical fitting equations which we believe will also apply to substituents not included in the current data set.

Method of Calculation

Adiabatic ionization potentials for disubstituted benzene molecules were calculated at $T = 0$ K. The method used to obtain ionization potentials was described in detail in ref 14. Briefly, for all molecules and ions, global minimum geometries were determined using the AM1[15] method, as implemented in the Spartan 5.0 package.[18] Zero-point vibration frequencies

were also calculated at the AM1 level and scaled by a factor of 0.973, as reported in ref 7a. The AM1 geometries were used to evaluate the single-point electronic energies at the (U)-B3LYP/6-31G(d) level,[16] where (U) denotes that an unrestricted open-shell treatment is used for the cations. The electronic energies and scaled zero-point energies were summed to obtain E_0, the total energy at 0 K. Ionization potentials (IP) were then determined by E_0(cation) $- E_0$(parent). Values that are expressed relative to the benzene molecule are denoted $\Delta IP = IP$(molecule) $- IP$(benzene).[14] All single-point energy calculations were performed using the Gaussian-94 package.[19]

Results

The relative ionization potentials (ΔIPs) for 55 para- and 55 meta-disubstituted benzenes are listed in Table 1 along with the available experimental values. The errors associated with the experimental values are typically less than 1 kcal/mol. These sets of compounds consist of all the binary combinations of 10 substituents. The set of substituents contains four representative electron-withdrawing groups ($-NO_2$, $-CF_3$, $-CHO$, $-COOH$) and six electron-donating groups ($-Cl$, $-CH_3$, $-OH$, $-OCH_3$, $-NH_2$, $-N(CH_3)_2$). The data in Table 1 are arranged in order of increasing ΔIP. The calculated and experimental reference IPs for benzene are 202.1[14] and 213.163 $\pm$ 0.001[20] kcal/mol, respectively. The two reference values differ by almost 11 kcal/mol, but as discussed previously,[14] the absolute error in calculated IP is fairly constant over the series of substituted benzenes and effectively cancels out in determining ΔIP.

For the para-disubstituted benzenes, generally excellent agreement between calculated and experimental ΔIPs is observed. The mean absolute deviation (MAD) between ΔIP values is 3.64 kcal/mol (0.16 eV) for the 41 compounds for which experimental data are available, where the ΔIP values span a range of over 100 kcal/mol. The bulk of the MAD can be attributed to a few compounds: Computed values for *p*-methoxybenzoic acid, *p*-hydroxybenzoic acid, and *p*-hydroxybenzaldehyde deviate from experiment by 12.8, 11.2, and 11.3 kcal/mol, respectively; i.e., the absolute IP (expt) is much higher than the IP (calcd). Two other compounds (*p*-(trifluoromethyl)chlorobenzene and *p,p*-bis(trifluoromethyl)benzene) have ΔIP values that deviate, in the same manner, by 6−7 kcal/mol. All of these particular experimental values were determined using electron impact,[21] a technique that has been shown to predict ionization potentials that are typically too high.[9b] Removing the ionization potentials for these compounds and reevaluating the deviation results in an improved MAD value of 2.82 kcal/mol. The computed ΔIP values for both *p*-dimethylaminobenzoic acid and *p*-dimethylaminobenzaldehyde are higher than the experimental values by 10.5 and 7.9 kcal/mol, respectively. For these two cases, the experimental values were obtained from photoelectron spectroscopy.[22]

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Table 1. Calculated and Experimental Gas-Phase Ionization Potentials for Disubstituted Benzene Molecules at 0 K, Relative to Benzene (ΔIP) (All Values in kcal/mol)

substituent 1	substituent 2	para substituted		meta substituted	
		calcd[a]	expt[b]	calcd[a]	expt[b]
N(CH₃)₂	N(CH₃)₂	−71.1	−70.2	−61.5	
N(CH₃)₂	NH₂	−66.0	−64.2	−55.5	
NH₂	NH₂	−60.0	−55.9	−49.1	−48.5
N(CH₃)₂	OCH₃	−58.0	−58.7	−49.0	
N(CH₃)₂	OH	−55.5		−47.9	
N(CH₃)₂	CH₃	−51.7	−52.9	−49.3	−51.3
NH₂	OCH₃	−50.5	−49.9	−43.0	−34.2
NH₂	OH	−47.4		−39.3	
N(CH₃)₂	Cl	−44.7	−47.1	−40.9	−43.0
NH₂	CH₃	−42.7	−43.2	−39.4	−39.3
OCH₃	OCH₃	−40.6	−39.5	−32.6	−24.8
N(CH₃)₂	COOH	−38.9	−49.4	−41.9	
N(CH₃)₂	CHO	−36.9	−44.8	−39.9	
OCH₃	OH	−36.7	−40.2	−39.6	
N(CH₃)₂	CF₃	−36.2		−37.8	
NH₂	Cl	−35.2	−34.0	−30.6	−26.6
OH	OH	−32.4	−30.3	−24.5	−24.1
OCH₃	CH₃	−31.1	−31.0	−28.6	−28.7
N(CH₃)₂	NO₂	−29.0		−32.7	
NH₂	COOH	−28.7	−33.3	−30.8	−33.3
NH₂	CHO	−26.5	−22.9	−27.9	
OH	CH₃	−26.3	−25.7	−23.3	−20.4
NH₂	CF₃	−25.2		−26.5	
OCH₃	Cl	−23.9	−22.9	−20.0	−12.1
CH₃	CH₃	−19.3	−18.6	−17.2	−16.0
OH	Cl	−18.8		−14.4	−13.6
NH₂	NO₂	−17.6	−14.4	−20.9	−21.5
OCH₃	COOH	−17.5	−4.7	−18.8	−4.2
OCH₃	CHO	−15.5		−15.3	
OCH₃	CF₃	−13.2		−14.0	
CH₃	Cl	−12.1	−12.6	−9.4	−13.2
OH	COOH	−11.7	−0.5	−12.4	−1.0
OH	CHO	−9.6	1.7	−9.2	
OH	CF₃	−7.0		−7.9	
OCH₃	NO₂	−5.8	−10.5	−8.1	−12.5
Cl	Cl	−5.3	−6.3	−1.7	−3.3
CH₃	COOH	−4.8	−0.3	−5.2	4.3
CH₃	CHO	−2.6	2.0	−1.3	
CH₃	CF₃	0.5		0.1	
OH	NO₂	0.8	−3.3	−1.5	−5.6
Cl	COOH	1.8		1.2	
Cl	CHO	3.9	8.4	3.9	
Cl	CF₃	6.9	13.3	6.4	11.9
CH₃	NO₂	9.9	5.0	6.4	4.8
COOH	COOH	10.0	14.2	12.4	17.0
COOH	CHO	13.2		11.3	
Cl	NO₂	14.0	16.5	12.3	15.6
COOH	CF₃	15.1		14.9	
CHO	CHO	15.6	20.4	10.7	
CHO	CF₃	16.4		17.2	
CF₃	CF₃	20.9	27.4	20.3	
COOH	NO₂	21.1	21.6	22.5	24.6
CHO	NO₂	22.2	23.6	20.6	
NO₂	CF₃	26.8	25.1	26.4	
NO₂	NO₂	33.8	29.0	32.5	26.7
MAD relative to experiment (N)			3.64(41)		4.08 (28)

[a] Referred to calculated IP of benzene, 202.1 kcal/mol.[14] [b] Referred to experimental IP of benzene, 213.163 kcal/mol.[20] Experimental data from ref 23.

However, analyses based on additivity of ΔIPs (see below) suggests that the experimental values are underestimated. The remaining calculated data are within 5 kcal/mol of the corresponding experimental values.

For the meta-disubstituted benzenes, only 28 experimental values were available for comparison. The MAD of 4.08 kcal/mol for this set is somewhat higher than for
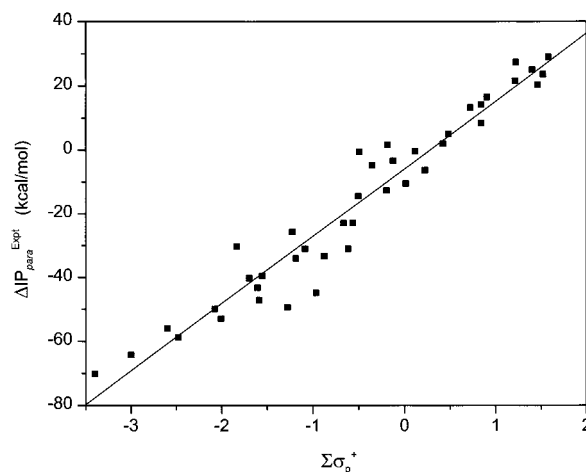
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Figure 1. Plot of experimental relative ionization potential (ΔIP) vs the sum of the Hammett substituent parameters, $\Sigma\sigma_p^+$, for para-disubstituted benzenes.

the para-disubstituted data. Inspection of the data shows that two ΔIP values are in disagreement by more than 10 kcal/mol. The deviations in ΔIP for *m*-methoxybenzoic acid and *m*-hydroxybenzoic acid are 12.6 and 11.4 kcal/mol, respectively (cf. 12.8 and 11.2 for the para species). Of the remaining 26 molecules, four compounds (*m*-dimethoxybenzene, *m*-chloroanisole, *m*-methylbenzoic acid, and *m*-(trifluoromethyl)chlorobenzene) have ΔIP values that are too low by 5−10 kcal/mol. In each of these cases, the experimental values were determined using electron impact.[21a,21b] The MAD for the meta set of data without these six outliers improves to 2.70 kcal/mol. The remaining data agree to within 5 kcal/mol of experiment.

Correlation Analysis: Predicting ΔIP. For the purpose of developing predictive models, it is of interest to examine the relationship between ΔIP and substituent parameters. In Figure 1, a plot of experimental ΔIP versus the sum of $\Sigma\sigma_p^+$, the Hammett substituent parameters,[6] is shown for the para-disubstituted benzenes. As can be seen from Figure 1, there is a significant correlation between ΔIP and $\Sigma\sigma_p^+$. A linear, least-squares fit of the data gives the relationship

$$\Delta IP_{para}{}^{expt} = 21.10\Sigma\sigma_p^+ - 5.89 \text{ kcal/mol} \qquad (1)$$

with a correlation coefficient of 0.94 and a standard deviation of 7.21 kcal/mol. The result of the least-squares fit (eq 1) indicates that, while the correlation coefficient is fairly high, the derived relationship cannot be used to predict accurate ΔIP values because of the large standard deviation. This was recognized by Bentley and Johnstone,[9b] who developed a "σ_{IP}" scale from their experimental vertical ionization potential data for monosubstituted benzenes. In that work, the authors derived a fitting function for the ionization potential of para-disubstituted benzenes that contained an additive term ($\sigma_{IP1} + \sigma_{IP2}$) and a correction term of the form $|\sigma_{IP1} \times \sigma_{IP2}|$ that becomes dominant when both σ_{IP1} and σ_{IP2} (or, equivalently, ΔIP_1 and ΔIP_2) become large. They found that this function reproduced the vertical ionization potential fairly well for 14 disubstituted benzenes and that the correction term significantly improved the fit.

We could take a similar approach to that of Bentley and Johnstone and derive a σ_{IP} scale based on experimental adiabatic ionization potentials. However, rather

Table 2. Calculated and Experimental Relative Ionization Potentials (ΔIP) for 10 Monosubstituted Benzenes (Data from Ref 14, in kcal/mol)

substituent	calcd[a] ΔIP	exptl[a] ΔIP
$N(CH_3)_2$	−46.5	−49.0
NH_2	−36.0	−35.1
OCH_3	−23.7	−23.8
OH	−18.0	−17.0
CH_3	−10.3	−9.6
Cl	−3.1	−4.2
COOH	5.7	5.2
CHO	5.9	5.7
CF_3	11.1	10.3
NO_2	17.5	15.8

[a] See Table 1 for details on reference energies for benzene.
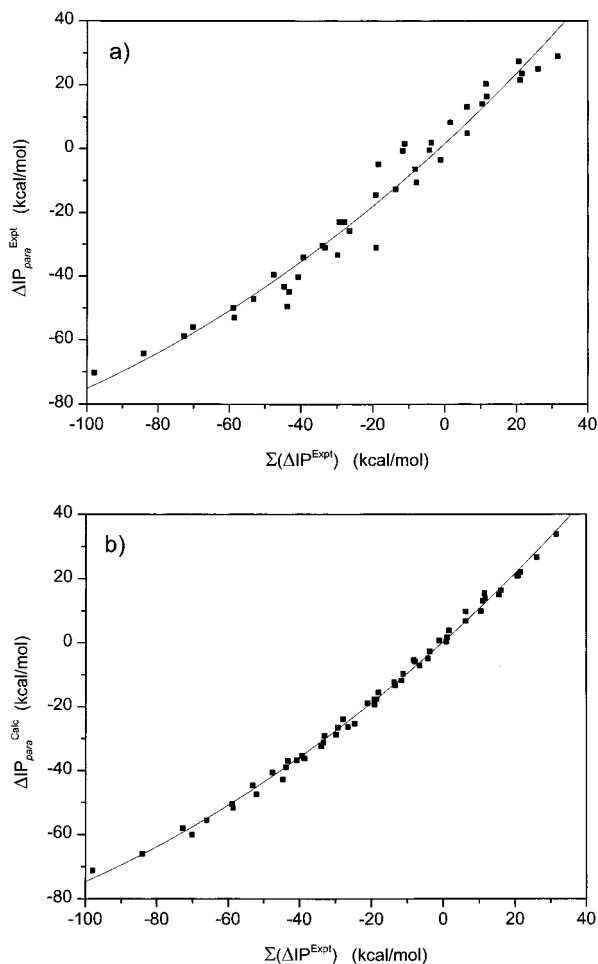
Figure 2. Plot of experimental (a) and calculated (b) para-disubstituted benzene relative ionization potentials vs the sum of experimental monosubstituted benzene relative ionization potentials.

than introduce yet another Hammett parameter into the literature, a more direct approach is simply to fit the present ΔIP data using monosubstituted ionization potentials, also expressed as ΔIPs. These are taken from ref 14 and listed in Table 2. If desired, these ΔIP data could be converted into a σ_{IP} scale.

The experimental para-disubstituted ΔIP data (Table 1) are plotted in Figure 2a as a function of the sum of the experimental monosubstituted ΔIPs listed in Table 2. An examination of Figure 2a shows that the para-disubstituted ΔIP data are somewhat scattered, but there appears to be a nonlinear relationship with the sum of

the monosubstituted ΔIPs. Least-squares fitting marginally supports this observation, with a quadratic function (shown in Figure 2a) yielding a slightly lower standard deviation than a linear function (5.50 vs 6.27 kcal/mol, respectively). However, given the scatter in the experimental data, it is suggestive but not conclusive that the true relationship is nonlinear.

Figure 2b shows the *calculated* para-disubstituted benzene ΔIP data, also plotted against the sum of experimental monosubstituted ΔIPs. In Figure 2b, owing to the greatly reduced scatter, a quadratic relationship between the two quantities clearly emerges. The calculated ΔIP data, in kcal/mol, are fitted according to

$$\Delta IP_{para}^{calcd} = 2.58 \times 10^{-3} (\Delta IP_1^{expt} + \Delta IP_2^{expt})^2 + 1.010 (\Delta IP_1^{expt} + \Delta IP_2^{expt}) + 0.44 \quad (2)$$

resulting in a very high correlation coefficient of 0.998 and a remarkably low standard deviation of 1.55 kcal/mol. This function also contains cross terms of the form $(\Delta IP_1 \times \Delta IP_2)$ similar to Bentley and Johnstone[9b] as well as the diagonal terms in $(\Delta IP_1)^2$ and $(\Delta IP_1)^2$. It is clear from these data fits that while the experimental data show considerable scatter, the calculated para-disubstituted ΔIPs show so little scatter that a definitive relationship with the sum of experimental monosubstituted ΔIPs can be derived. The relationship is quadratic, showing significant curvature near the low end of the data range.

In Figure 2b, we used the experimental ΔIP data on monosubstituted benzene, combined with calculated ΔIP data for the disubstituted benzene, to establish the correlation in eq 2. Calculated monosubstituted benzene ΔIP values may also be used to predict calculated ΔIP_{para} results. These data, calculated by the same methodology as in ref 14, are reproduced for convenience here in Table 2. A least-squares fit using the calculated monosubstituted data listed in Table 2 yields the relationship (in kcal/mol)

$$\Delta IP_{para}^{calcd} = 1.92 \times 10^{-3} (\Delta IP_1^{calcd} + \Delta IP_2^{calcd})^2 + 0.965 (\Delta IP_1^{calcd} + \Delta IP_2^{calcd}) - 0.390 \quad (3)$$

which gives a correlation coefficient of 0.998 and a standard deviation of 1.57 kcal/mol. The essentially identical agreement in the fitting of the data using either eq 2 or eq 3 suggests that either calculated or experimental monosubstituted benzene data may be used to obtain a para-disusbtituted benzene ΔIP with nearly the same predictive value. Note, however, that the purely calculated eq 3 shows less curvature (smaller quadratic term). This is mostly due to the different value for $N(CH_3)_2$ at the end of the range (−46.5 calcd, −49.0 expt, Table 2), so that the experimental value will amplify the curvature needed in eq 2 in order to minimize the least-squares deviation.

A similar approach can also be used to fit the meta-disubstituted benzene data in Table 1. In Figure 3, ΔIP_{meta}^{calcd} is plotted against the sum $(\Delta IP_1^{expt} + \Delta IP_2^{expt})$, where the latter are experimental values taken from Table 2. The data in Figure 3 show slightly more scatter than those in Figure 2b. This is reflected in the least-
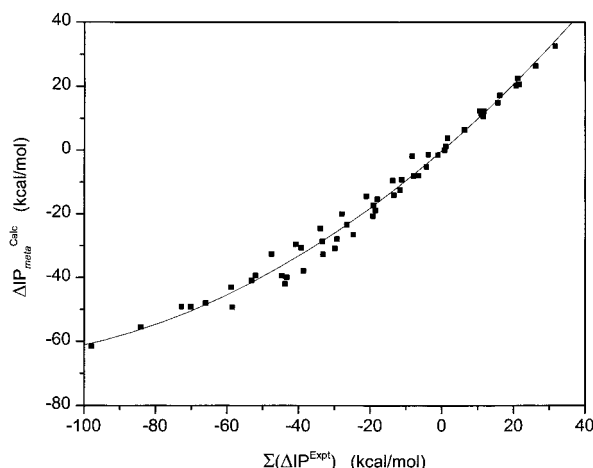
Figure 3. Plot of calculated meta-disubstituted ΔIPs versus the sum of experimental monosubstituted benzene ΔIP.

squares fit to eq 4 (in kcal/mol)

$$\Delta IP_{meta}^{\ calcd} = (3.60 \times 10^{-3})(\Delta IP_1^{\ expt} + \Delta IP_2^{\ expt})^2 + 0.970(\Delta IP_1^{\ expt} + \Delta IP_2^{\ expt}) - 0.13 \quad (4)$$

which yields a standard deviation of 2.85 kcal/mol. Note that the coefficient of the second-order term (3.60×10^{-3}) of eq 4 for meta compounds is much higher than that in the function for para compounds $(2.58 \times 10^{-3}$, eq 2) which will become important in the discussion of additivity to follow.

The use of calculated monosubstituted benzene ΔIP data (Table 2) gives (in kcal/mol)

$$\Delta IP_{meta}^{\ calcd} = (3.11 \times 10^{-3})(\Delta IP_1^{\ calcd} + \Delta IP_2^{\ calcd})^2 + 0.929 (\Delta IP_1^{\ calcd} + \Delta IP_2^{\ calcd}) - 1.06 \quad (5)$$

and fits the data with a slightly larger standard deviation of 3.32 kcal/mol. The two fits are close enough, however, that we may conclude that the use of monosubstituted benzene ΔIP values from either experiment or calculation will yield reasonably accurate meta-disubstituted benzene ΔIPs.

For both para- and meta-disubstuted benzenes, then, the derived empirical models for ΔIP clearly show a quadratic relationship with the sum of the ΔIPs of the respective monosubstituted benzenes (experimental or calculated). These models span a wide range of electron-donating and electron-withdrawing substituents and provide fits to the calculated data with high enough accuracy that ionization potentials may be predicted for disubstituted benzenes containing substituents *that are not in the calibration set,* using only the derived eqs 2−5.

For example, consider *p-tert*-butyl- and *p*-cyanobenzene for which predicted and experimental ΔIPs are listed in Table 3. Using eq 2, both the para-substituted *tert*-butylbenzene and cyanobenzene ΔIPs are in generally good agreement with available experimental data. For the 19 available experimental values, the mean absolute deviation from experiment is 3.0 kcal/mol. (The uncertain experimental value for *p*-cyanobenzaldehyde was not included in the evaluation of the MAD.) The largest disagreements between predicted and experimental ΔIPs are observed for *p*-(trifluormethyl)cyanobenzene, *para*-hydroxycyanobenzene and *p*-chlorocyanobenzene, where

Table 3.   Predicted (Eq 2) and Experimental ΔIPs for Para-Substituted Cyano and *t*-Butyl Groups (All Values in kcal/mol)

molecule	para substituent	ΔIP	
		eq 2	expt[b]
tert-butylbenzene	N(CH₃)₂	−51.8	−54.0
	NH₂	−42.2	−43.7
	OCH₃	−33.6	−34.0
	OH	−28.0	−33.3
	C(CH₃)₃[a]	−25.4	−23.1
	CH₃	−21.7	−22.2
	Cl	−16.9	−15.8
	COOH	−8.1	−7.0
	CHO	−7.7	
	CN	−2.3	−3.1
	NO₂	2.4	
	CF₃	3.2	
cyanobenzene	N(CH₃)₂	−33.7	−37.9
	NH₂	−22.1	−24.8
	OCH₃	−11.8	−14.8
	OH	−5.3	3.6
	CH₃	2.1	1.8
	Cl	7.6	16.1
	COOH	17.8	17.4
	CHO	18.3	≤19.7
	CF₃	23.5	31.5
	CN[a]	24.5	19.7
	NO₂	29.8	31.0

[a] The experimental ΔIP values for these substituents are taken from ref 14. [b] Reference 23.

experimental values are higher by 8.9, 8.5, and 8.5 kcal/mol, respectively. These experimental values were determined using electron impact studies[24] and, as discussed previously, are considered to be high. Discarding these three values, the MAD improves to 1.9 kcal/mol.

A detailed comparison between experimental and calculated ΔIPs for the meta-disubstituted benzenes was not possible, owing to the scarcity of experimental data. We did calculate such data theoretically and discrepancies were noted with existing experimental data. However, for all the meta-disubstituted values that were in significant disagreement with experiment, the experimental ionization potentials were determined using electron impact studies.

Qualitative Trends in Monosubstituted Benzene. Figure 2b shows that the relationship between $\Delta IP_{para}^{\ calcd}$ and the sum of the experimental, monosubstituted ΔIP values is linear, with a slope near 1.0 and an intercept near zero, over the range $-30 < (\Delta IP_1 + \Delta IP_2) < +30$ kcal/mol. Therefore, a good approximation to $\Delta IP_{para}^{\ calcd}$ for relative ionization potentials in this range can be made by simply summing $\Delta IP_1 + \Delta IP_2$ from experimental values for the corresponding monosubstituted benzenes. Outside this range, the relationship becomes quadratic, in particular for values of $(\Delta IP_1 + \Delta IP_2)$ more negative than −30 kcal/mol, i.e., near the low end of the range. Equation 2 shows the relative importance of the linear and the quadratic term, and at a value $(\Delta IP_1 + \Delta IP_2) = -30$ kcal/mol, the magnitude of the quadratic term is ca. 3 kcal/mol. Outside this range, the quadratic dependence begins to clearly manifest itself above the scatter in the data.

To have a qualitative understanding of the trends in ΔIP, perturbation molecular orbital (PMO) arguments

(23) National Institute of Standards and Technology on-line database. Standard Reference Data Program 69, November 1998 Release. http://webbook.nist.gov.
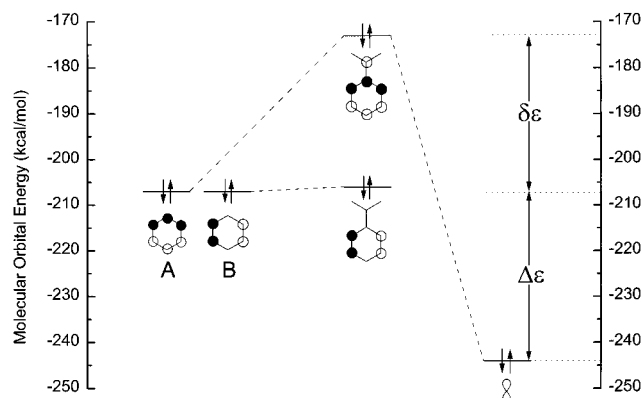(24) Buchs, A. *Helv. Chim. Acta* **1970**, *53*, 2026.

Figure 4. MO diagram for addition of an $-NH_2$ group (strongly electron-donating) to benzene. See text for definition of $\Delta\epsilon$ and $\delta\epsilon$.

can be used.[3,4] In this paper, we use the actual orbital energies obtained for benzene substituted with an electron-donating group (EDG) or electron-withdrawing group (EWG) or with combinations of both substituents. For this purpose, we used Hartree−Fock SCF calculations with a 6-31G(d) basis set.

Case of an EDG. Consider first an EDG, a representative example of which is an amino group, which has a substantial effect on the IP. The energy separation between the filled benzene HOMO and the filled amino p-orbital is defined to be $\Delta\epsilon$. Due to the filled−filled interaction, the destabilization of the resulting antibonding orbital, $\delta\epsilon$, is inversely proportional to the energy separation between the filled MO's.[25] Figure 4 shows this interaction between the benzene HOMO of the correct symmetry ("A" on the diagram) with the filled p-orbital on NH_2. The benzene HOMO lies at -207 kcal/mol from our calculation. The energy of the interacting p-orbital on nitrogen was obtained from an SCF calculation on the $^2A_1$ state of NH_2, and it lies below the benzene HOMO at -244 kcal/mol. The energy separation between the filled MO's ($\Delta\epsilon$) is therefore 37 kcal/mol. As a result of the interaction the bonding combination is stabilized (not shown) and the less-bonding combination (center of diagram) is destabilized; the latter becomes the HOMO of aniline at -173 kcal/mol, giving $\delta\epsilon = 34$ kcal/mol. Using Koopman's theorem, this value for $\delta\epsilon$ is consistent with the observed change in IP (35 kcal/mol) for the amino substituent (Table 2).

Figure 4 also shows that the formerly degenerate benzene HOMO ("B") is slightly raised relative to benzene. This results since the amino group donates electrons to the ring which then becomes partially negatively charged, thus raising the energy of the entire manifold of MOs (i.e., a "shielding" affect, as discussed by Pross and Radom[4]). The net effect is small, however, because the π-donation is partially offset by electron withdrawal into the C−N σ bond. Note that a small decrease in the aniline ionization potential (about 1 kcal/mol) is found when the amino group is rotated such that the nitrogen lone-pair is in the plane of the ring.

Figure 4 can also be used to clarify the trend in ΔIPs shown in Table 2 for other monosubstituted benzenes. For an electron-donating group X, the substituent has a HOMO that in general lies below that of the benzene

(25) McQuarrie, D. A. *Quantum Chemistry*; University Science Books: Mill Valley, CA, 1983.

Table 4. Nonconjugated and Conjugated Electron-Withdrawing Group Effects on the HOMO and HOMO-1 of Monosubstituted Benzene (Values Are in kcal/mol)

substit-uent	nonconjugated		conjugated		ΔIP
	ϵ(HOMO)	ϵ(HOMO-1)	ϵ(HOMO)	ϵ(HOMO-1)	
NO_2	-230	-230	-230	-235	$+17.5$
CF_3	-223^a	-228^a	-223	-228	$+11.1$
CHO	-217	-218	-217	-220	$+5.9$
COOH	-219	-220	-219	-222	$+5.7$

^{a} The CF_3 group cannot be oriented so that no conjugation occurs since conjugation arises from the linear combination of virtual σ_{C-F} orbitals.

HOMO. Assuming that the overlap between the p-orbitals through the C−X bond for the other substituents (e.g., −OH, $-OCH_3$, $-CH_3$) is similar to that in aniline,[26] the destabilization caused by substituent X is related to that of the amino group by

$$\delta(X) = \delta(NH_2)[\Delta\epsilon(NH_2)/\Delta\epsilon(X)] \qquad (6)$$

Using this relationship, the orbital energy of the relevant substituent HOMO was taken to be the highest-lying filled MO of π-type symmetry. These were obtained from calculations on the electronic states $^2A'$ for OCH_3, $^2\Sigma$ for OH, and $^2A'$ for CH_3; in each of these states, the odd electron is in a σ-orbital so that the highest doubly occupied MO will be of π-symmetry. The Hartree−Fock MO energies are -261, -290, and -340 kcal/mol for methoxyl, hydroxyl, and methyl, respectively. Note that these HOMO energies follow the trend expected[6] for electron-donating groups that are weaker than the amino group.[27] The MO energy differences between filled MO's, $\Delta\epsilon$(X), therefore vary as 54, 83, and 133 kcal/mol for methoxyl, hydroxyl, and methyl groups, respectively. Using eq 6, the destabilization of the HOMO of the substituted benzene relative to benzene is -23.3 (anisole), -15.0 (phenol), and -9.5 (toluene) kcal/mol, in excellent agreement with the calculated values listed in Table 2.[28]

Case of an EWG. For electron-withdrawing groups, PMO analysis has usually invoked the HOMO−LUMO interaction to explain substituent effects, where the LUMO is the substituent π^* system. However, we find that the EWG effect on IP is essentially completely the result of σ-inductive (and hence deshielding) effects. This can be seen by examining the effect on HOMO energies in both nonconjugated and conjugated EWG-substituted benzenes as compiled in Table 4. For Table 4, conjugated groups (e.g., NO_2) are coplanar with the ring, whereas nonconjugated groups are rotated by 90°.

As shown in Table 4, the addition of an EWG to benzene in nonconjugated mode results in monosubsti-

(26) The bond distances between the aryl carbon and the carbon or oxygen atoms of the substituents varies by less than 0.1 Å, which indicates that p-orbital overlap should be relatively constant for the amino, methoxyl, hydroxyl, and methyl substituents. The given analysis cannot be applied to chlorobenzene because the C−Cl bond length is significantly larger than the C−X bond lengths in the other benzenes substituted with electron-donating groups.

(27) In this case the methyl HOMO lies lowest because it is a combination of CH bond orbitals of π-symmetry, i.e., $2\sigma_1 - \sigma_2 - \sigma_3$. Since this contains C−H sigma-bonding character it lies relatively low in energy, compared to the amino and hydroxyl orbitals which are pure 2p.

(28) Note that we have omitted the $-N(CH_3)_2$ from this discussion. The HOMO energy of this substituent is -204 kcal/mol, making it nearly degenerate with the HOMO's of benzene. In cases of near degeneracy, the relationship expressed in eq 6 is invalid.

tuted benzenes that still have a degenerate pair of MO's. The energy of the (degenerate) HOMO in each case is lowered relative to benzene by an amount that follows the trend expected with decreasing strength of EWG.[6] Rotating the substituent to coplanarity with the ring (conjugated mode) removes the degeneracy between the HOMO orbitals through an interaction with one member of the degenerate pair. The interaction now occurs between the LUMO on the substituent and a filled HOMO of benzene and lowers the energy of the resultant MO; this becomes HOMO-1. The noninteracting HOMO orbital is unaffected by this mixing, and its energy is unchanged relative to the nonconjugated mode. Since the HOMO energy of the monosubstituted benzenes is unchanged with respect to the degree of conjugation, the effect of electron-withdrawing groups on ionization potential must be due to the energy lowering (contraction) of ring π-orbitals in response to the deshielding caused by σ-inductive effects.

Disubstituted Benzene. EWG−EWG. For the disubstituted benzenes, the general trends in ΔIP can be understood using an extension of the arguments given for monosubstituted benzenes. For example, since the addition of an EWG to benzene lowers the HOMO energy (and therefore the ΔIP) through a deshielding mechanism, the addition of a second EWG must lower the HOMO energy by the same mechanism. Comparisons of the Mulliken charges on EWG monosubstituted benzene relative to the unsubstituted molecule show very little change in charge distribution at the unsubstituted sites. This implies that, regardless of where substitution occurs, the addition of a second EWG to molecules of this type will have essentially the same effect on the HOMO energy as the first. Consequently, both ΔIP$_{para}^{calcd}$ and ΔIP$_{meta}^{calcd}$ values for benzenes disubstituted with EWGs should be well approximated by (ΔIP$_1$ + ΔIP$_2$). For the 10 such compounds listed in Table 1, this is found to be the case: The mean absolute deviation between ΔIP$_{para}^{calcd}$ and (ΔIP$_1$ + ΔIP$_2$) for these species is less than 1.7 kcal/mol, while a similar evaluation for ΔIP$_{meta}^{calcd}$ gives an MAD of 1.5 kcal/mol. This can be understood if the substituent effects on the HOMO of monsubstituted benzene are purely inductive, as in the case of a mono-EWG-substituted benzene. In other words, there is no discrimination between positions, and meta and para substituents become equivalent in their effect on IP.

EDG−EWG. A similar comparison of the charges on EDG monosubstituted benzenes also indicates very little change in charge distribution at the unsubstituted sites. We therefore expect that the addition of an electron-withdrawing group, regardless of position, to EDG monosubstituted benzenes will lower the energies of the HOMOs to the same extent as that which occurs in EWG monosubstituted benzenes. That is, any disubstituted benzene that contains one electron-donating and one electron-withdrawing group should have a relative ionization potential that is additive. The 24 compounds listed in Table 1 that contain one of each type of substituent have ΔIP$_{para}^{calcd}$ values that deviate from additivity by an MAD of only 1.21 kcal/mol. Furthermore, the ΔIP$_{para}^{calcd}$ and ΔIP$_{meta}^{calcd}$ values for the EWG−EDG case have an MAD between themselves of only 1.46 kcal/mol, i.e., there is no discrimination either, in this case of EWG−EDG, between meta and para substituents. The

Table 5. Relative Ionization Potentials for Electron-Donating Group Monosubstituted Benzenes (All Values are in kcal/mol)[a]

substituent	ΔIP(mono)[b]	$\Delta\epsilon_2$[c]	δ(eq 6)	ΔIP$_{para}^{calc}$ [d]	ΔIP(add)[e]
Cl	−3.1	33.9	37.1	−35.2	−39.1
CH$_3$	−10.3	47.3	26.6	−42.7	−46.3
OH	−18.0	55.0	22.9	−47.4	−54.0
OCH$_3$	−23.7	60.7	20.7	−50.5	−59.7
NH$_2$	−36.0	73.0	17.2	−60.0	−72.0
N(CH$_3$)$_2$	−46.5	83.5	15.1	−66.0	−82.5

[a] Also shown are the orbital energy differences between the monosubstituted benzene HOMO and the lone-pair orbital of the amino group. The relative destabilization of the resulting antibonding orbital is computed using eq 6. Calculated relative ionization potentials and those predicted by additivity are also shown. [b] Values taken from Table 2. [c] Energy separation between monosubstituted benzene HOMO and the amino group lone-pair. Koopman's theorem is used to estimate the energy of the HOMO. [d] Values from Table 1. [e] Relative ionization potentials predicted from additivity.

comparable effects of meta and para EWGs on bond dissociation enthalpies has been note by Bordwell et al.[29]

EDG−EDG, Para. Next, consider whether additivity should be observed in the case of two weakly electron-donating groups, e.g., methyl. Addition of a methyl group to benzene results in the HOMO in toluene being higher than that in benzene by about 10 kcal/mol (HF calculation). The energy separation between the doubly occupied toluene HOMO and the methyl group orbital ($\Delta\epsilon_2$) is then 143 kcal/mol, rather than the 133 kcal/mol ($\Delta\epsilon_1$) obtained previously for benzene. Since the energy splitting $\delta\epsilon$ that raises the toluene HOMO is inversely proportional to the separation between filled MOs and $\Delta\epsilon_2$ is the same as $\Delta\epsilon_1$ to within 7%, the effect on IP of the second substituent is very close to that of the first. The use of eq 6 in this case gives a $\delta\epsilon$ value of −9.5 kcal/mol for toluene and −8.8 kcal/mol for the para addition of the second methyl group. Since the destabilization of the HOMO orbitals is almost identical, additivity is expected to hold for this molecule. The ΔIP$_{para}^{calcd}$ for *p*-xylene is −19.3 kcal/mol while additivity predicts −20.3 kcal/mol.

Conversely, the addition of a strong EDG to benzene necessarily implies a small value for $\Delta\epsilon_1$. There will then be a large shift upward in the HOMO energy. The addition of a second strong EDG to the para position would now have a much larger $\Delta\epsilon_2$ and a corresponding smaller $\delta\epsilon$ value. In this case, additivity will no longer hold. This has been referred to as a "saturation" effect in the literature.[4] This effect is readily observed in the deviation from additivity associated with the addition an amino group (strong EDG) to various monosubstituted benzenes. The data in Table 5 illustrate the saturation effect in benzenes substituted with two electron-donating groups. The second column of the Table contains the EDG monosubstituted benzene ΔIP values from Table 2 for ease of comparison. Using these values to estimate the monosubstituted benzene HOMO energy, $\Delta\epsilon_2$ values can be calculated based on the orbital energy of −244 kcal/mol for the amino group. Equation 6 is used to compute the destabilization of the resulting HOMO upon the addition of the amino group to the para position of the monosubstituted benzene. For the formation of aniline from benzene and the amino group, the $\Delta\epsilon_1$ value is 37 kcal/mol and the corresponding $\delta\epsilon$ value is 34 kcal/mol.

(29) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 6605.

The latter quantity can be compared to the $\delta\epsilon$ values presented in Table 5 to determine the degree of the saturation effect in the substituted benzene. As the strength of the electron-donating substituent increases, $\Delta\epsilon_2$ becomes large and the mixing between the monosubstituted HOMO and the amino group orbital becomes weaker. The δ values reflect the weaker interactions by decreasing with increasing $\Delta\epsilon_2$ and display larger deviations from the idealized value of 34 kcal/mol in aniline with the strength of the electron-donating group. The deviation from additivity increases from about 4 kcal/mol in *p*-chloroaniline to nearly 17 kcal/mol for *p-N,N*-dimethylaminoaniline.

EDG−EDG, Meta. In the case of the meta addition of strong EDGs, larger deviations from additivity are generally observed. In the case of *m*-diaminobenzene, for example, the calculated value of −49.1 kcal/mol (Table 1) shows a large deviation of 23 kcal/mol from the sum of individual values, compared to a deviation of 12 kcal/mol for *p*-diaminobenzene (Table 5). Figure 5 shows the relevant interactions for meta (right) and includes para (left) for comparison. The para interaction, discussed previously, is relatively simple: the amino p-orbital interacts with the HOMO in aniline creating a new HOMO (top left). The meta interaction is more complicated, however. The HOMO in *meta*-diaminobenzene (top right) has the node shifted relative to aniline, as required by symmetry, with an antibonding interaction between the nitrogen p-orbital and the ring. Such a nodal structure can only be created by combining the HOMO and the HOMO-1 in aniline, which can be seen by adding the two MO's. A reference point for the aniline MO is therefore *the mean value* of these two MO's (center dashed line, Figure 5), i.e., considerably lower than the HOMO in aniline used in the *para*-case. The filled-filled interaction ($\Delta\epsilon$) is reduced, leading to a stronger mixing for meta than for para. This is clearly outweighed, however, by lowering the starting position (i.e., to the mean value) of the respective aniline MO. The final HOMO in *m*-diaminobenzene lies much lower than expected if additivity were observed. The strong curvature evident in Figure 3, compared to the weaker curvature in Figure 2b, shows greater deviation from additivity is present in the meta case than in the para case.

More than Two Substituents. The discussion given for two substituents should, in principle, be extendable to the case of polysubstituted benzenes. We have seen significant nonadditivity in the case of hexamethylbenzene in previous work.[14] This suggest that saturation effects will be observed even though approximate additivity holds in *m*-xylene and *p*-xylene. Analysis of the sources of this nonadditivity will become more difficult due to the more complicated orbital mixing associated with presence of multiple substitutents. Whether or not a simple quadratic relationship between polysubstituted ΔIPs and the sum of monosubstituted ΔIPs holds remains to be established.

Conclusions

In this paper, we have given calculated values for relative ionization potentials (ΔIP) for 55 para- and 55 meta-substituted benzenes, using density functional theory with the B3LYP functional and a 6-31G(d) basis set. The set of substitutents included four electron-
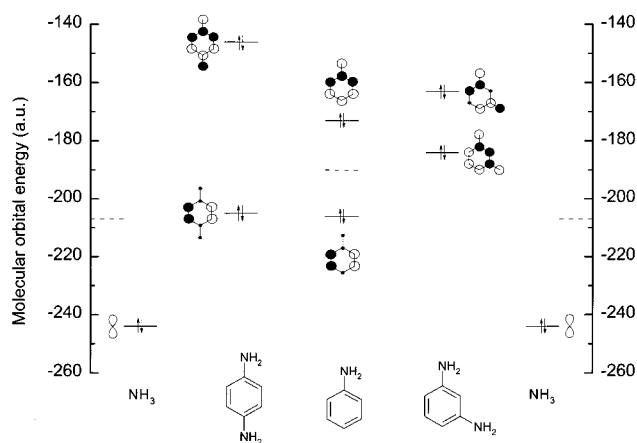

Figure 5. Perturbative molecular orbital scheme for the para and meta addition of an −NH₂ group to aniline. The dotted lines represent the degenerate HOMO's for benzene. The dashed line represents the mean energy of the aniline HOMO and HOMO-1.

withdrawing groups (NO_2,CF_3, CHO, COOH) and six electron-donating groups (Cl, CH_3, OH, OCH_3, NH_2, and $N(CH_3)_2$). Calculated ΔIP values were obtained with respect to 202.1 kcal/mol, the calculated value for benzene. Experimental ΔIP values, obtained with respect to the experimental benzene reference value of 213.163 ± 0.001 kcal/mol, were compared to the calculated ΔIPs. Calculated data gave mean absolute deviations from available experimental values of 3.6 (para) and 4.1 kcal/mol (meta). The MADs improved to about 2.8 kcal/mol for both para- and meta-substituted dibenzenes when experimental data obtained by electron-impact studies were removed from the evaluation. Fitting functions were derived for both para- and meta-disubstituted benzene, based on monosubstituted benzene ΔIPs. Using either experimental or calculated monosubstituted benzene ΔIPs, excellent correlations were obtained. For para-disubstituted benzenes, our calculated data gave a standard deviation of the fit below 2 kcal/mol, for data which span a range of ΔIP values over 100 kcal/mol. Fits of the meta-disubstituted benzenes gave a standard deviation below 3 kcal/mol. The very small scatter in the calculated values for both para and meta showed that the true correlation is unambiguously curvilinear, with a quadratic term of the form $(\Delta IP_1 + \Delta IP_2)^2$ sometimes making a significant contribution, especially in the case of two strong electron-donating groups.

Molecular orbital analyses were performed to help understand the trends in ΔIP for mono- and disubstituted benzenes. For electron-donating groups, the energy difference for the relevant filled-filled interaction ($\Delta\epsilon$) determines the splitting ($\delta\epsilon$) between the original HOMO in benzene and the new HOMO in the monosubstituted benzene. This is directly related to the change in ΔIP. We showed that for the electron-donating substituents the correct order in ΔIP is predicted semiquantitatively, since the change in ΔIP is related to the inverse of $\Delta\epsilon$. For this purpose, MO energies obtained from a Hartree−Fock calculation were used, but the order of the filled orbitals in amino, methoxyl, hydroxyl, and methyl was also discussed qualititively to provide a model for understanding the results.

The additivity of substituent effects was discussed in detail for disubstituted benzenes with two electron-withdrawing groups or one electron-withdrawing and one

electron-donating group. We showed that, because EWGs reduce the ionization potential of benzene through σ-inductive effects, additivity of the monosubstituted ΔIPs accurately predicts calculated, disubstituted ΔIPs for these types of compounds.

Additivity breaks down for disubstituted benzenes with two electron-donating groups. As the energy separation between interacting MOs increases, the mixing between monsubstituted benzene HOMOs and substituent orbitals decreases. This "saturation" effect was illustrated for a series of para-substituted anilines and clearly shows the increasing deviation from additivity with increasing strength of the electron-donating group. An MO analysis for meta-disubstituted benzene was also given, using similar arguments. In this case, the mixing is more complex since, to obtain the correct symmetry, the substituent HOMO must mix with two MOs in the monosubstituted benzene. When proper account is taken of that interaction, the correct qualitative interpretation of the ΔIP behavior is obtained.