J. Am. Chem. Soc. 1981, 103, 3777-3781

to the resonances of the free and the complexed cation, were obtained for solutions containing an excess of sodium salt. Occasionally the two resonances seemed to blend into one very broad signal; for example, the addition of C221 to a DMF solution of sodium tetraphenylborate results in only very small displacement of the ^{23}Na resonance although the half-height line width of the resonance broadens considerably.

The chemical shifts of the complexed Na^+ ion are given in Table III. It is immediately obvious that the shifts are very much dependent on the nature of the ligand, i.e., the shift moves downfield as the size of the central cavity decreases, indicating an increasing overlap of the donor orbitals of the ligands' heteroatoms with the outer orbitals of the Na^+ ion. Our results agree very well with those obtained by Lehn and Kintzinger in $MeOH-D_2O$ mixture.[23] In nearly all cases the chemical shift became constant at the 1:1 ligand/Na^+ mole ratio, indicating that the complexes are quite stable, i.e., $K_f > 10^4$. Only in the case of the $Na^+\cdot$C211 system in water did the chemical shift continue to change somewhat beyond the 1:1 mol ratio.

The formation constants ($\log K_f$) for $Na^+\cdot$C211, $Na^+\cdot$C221, $Na^+\cdot$C222B, and $Na^+\cdot$C222 complexes in water are 3.2, 5.4, 4.0, and 3.9, respectively.[24,25] The values should be considerably higher in nonaqueous solutions. It is obvious that the magnitude of the ^{23}Na paramagnetic shift of the complexed cation in not directly related to the stability of the complexes.

Our measurements indicate (Table III) that with all four cryptates the chemical shift of the *complexed* sodium ion does depend on the medium, albeit to a small extent. It is evident, therefore, that the solvent has an access to the complexed cation.

The space-filling model of C221 clearly shows that due to the different lengths of the polyether strands, the ligand has an "open face" and that even when the cation is located in the center of the cavity, it remains somewhat exposed to the solvent.

Similar small variations of the chemical shift are observed for the $Na^+\cdot$C222 and $Na^+\cdot$C222B complexes. In these cases the cavity sizes are larger than that of the cation and there may be some penetration of solvent molecules into the cavity. In the case of C211, where the cavity size is considerably smaller than the cation, not only do the chemical shifts vary with the solvent, but in addition, in solvents with low dielectric constants (pyridine and tetrahydrofuran) the shifts clearly vary with the counterion. Therefore, the anions must be in some contact with the complexed cation and form a "tight" ion pair.

This behavior is different from cases where the cryptand forms an effective insulating layer around the metal ion in the center of the cavity. For example, we have shown previously that for the $Li^+\cdot$C211 complex the ^{7}Li chemical shift of the comlexed cation is completely independent of the solvent.[26] The same behavior was observed for the ^{133}Cs chemical shift for the $Cs^+\cdot$C222 complex at low temperatures.[27–29]

Temperature dependence of the sodium-23 chemical shift for the $Na^+\cdot$C211, $Na^+\cdot$C221, and $Na^+\cdot$C222 complexes was studied in a number of solvents. In the first case, the lines became so broad at low temperatures that accurate measurements of the chemical shifts were not possible. In the other two systems, while measurements could be carried out down to ca. −70 °C, the ^{23}Na chemical shifts showed no tendency to converge at low temperatures.

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Ab Initio Modeling of Substituent Effects in Hammett Correlations

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Abstract: Substituent effects have been modeled with the use of minimum basis set ab initio techniques. Substituted benzenes were perturbed with pure point charges to model nonbonded reaction centers. Two point charges were used to model a pure dipolar "substituent". Most substituents have essentially the same polarizability and, therefore, are independent of reaction center charge type. Phenyl, ethynyl, sulfonyl, and (in the para position) cyano groups are more polarizable while hydrogen and fluoro groups are less polarizable than "normal" substituents and must be treated with care. Nitro, cyano, and sulfonyl groups lack a mesomeric contribution to the destabilization of a positive reaction center. The boro group, on the other hand, has a mesomeric contribution. The stabilizing effect of a phenyl substituent is undoubtedly due to the polarizability of the benzene ring. Unipolar groups, such as the ammonium group, show apparent interaction with the benzene ring and appear as strong π donors even though mesomeric interactions are minimal. There is a slightly larger inductive effect at the para position than at the meta position. The effect is so small, however, that corrections of σ_I values are not warranted. Comparisons with experimentally derived substituent constants show that Wepster's σ^n values are the best set of "normal" substituent constants while Yukawa's σ^0 values still contain some through-bond resonance effects.

Organic chemists have always been intrigued with the effects that structural modifications have on chemical reactivity. Years of experimental observation have led to many empirical relationships. Although these relationships have been known for many years, the actual mechanism by which a substituent modifies chemical reactivity has yet to be adequately described. Topsom,[1] in his recent review on the nature and analysis of electronic effects, describes seven mechanisms by which a substituent can transmit its electronic effects to the reaction site. Thus far, these effects have not been completely separated and are usually grouped into

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[1] R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 1 (1976).

two major catagories. The effects which stem from the substituent's polarity, namely the σ-inductive effect (I_σ), the field effect (F), the σ-induced π effect (π_σ), and the field-induced π effect (π_F), constitute one group, while the substituent's charge-transfer ability, namely the mesomeric effect (R) and the π-induced σ effect (σ_π), constitute the other group. Any additional effects, (e.g., repulsions between the π system and filled π orbitals on the substituent (π_{orb})) are absorbed into one of these two catagories. Numerous attempts have been made by many researchers to quantify these effects with mixed success.[2]

Some headway has been made recently with the appearance of structure–reactivity correlations in the gas phase which eliminate complicating solvent effects.[3] Semiempirical and minimum basis set ab initio[5] molecular orbital calculations on substituted benzene rings have also proven useful. Reynolds et al.[6] have used a minimum basis set approach to calculate theoretical field and resonance parameters which agree reasonably well with experimentally determined values.

One of the major problems involved in separating field and inductive effects from mesomeric effects is the extent to which the reaction center, or probe, interacts with the substituent. In para-disubstituted benzenes these interactions can be substantial, e.g., *p*-nitrophenol. Several investigations have been made in attempts to define substitutent constants for systems in which such interactions are small, e.g., Taft's[7] σ_I, Yukawa's[8] σ^0, Wepster's σ^n,[9] and Exner's[10] corrected σ_I values. Inconsistencies between the scales appear to be a consequence of how well the interactions have been eliminated.[11] Minimum basis set ab initio molecular orbital theory can be applied to this problem. Substituent effects can be investigated by using point charge perturbations to model nonbonded reaction centers as probes. Two point charges can be used to model a pure dipolar substituent. The advantages include elimination of direct resonance interactions and the ability to rotate a substituent containing a π system or lone pair so that it either can, or cannot, interact with the benzene ring.

Methods

Calculations were performed on modified versions of the Gaussian-70 series of computer programs[12] and the HONDO program (version-5[13] at the STO-3G, minimum basis level). d functions were added to sulfur and chlorine atoms. Both of these programs have been modified to allow for storage and reuse of the two-electron integrals.[14] This is very convenient since the two-electron integrals do not change as perturbations are applied to the molecule. Moreover, additional savings were realized by reusing most of the two-electron integrals for substituent modifications. The HONDO program has been adapted for use on both a CDC 6400 and a DEC-20 computer system.

Table I. Energies (au) and Geometries for Substituted Benzenes

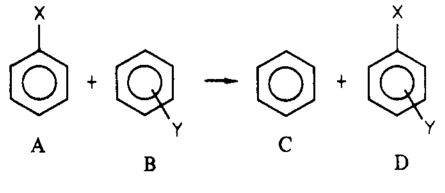
substituent	total energy	geometry of substituent[a]
$NO_2(\parallel)^b$	−428.57593	$r_{Ar-N} = 1.43; r_{N-O} = 1.21$
$NO_2(\perp)$	−428.56731	
dipole	−228.61432	$r_{H^+} = 1.0; r_{H^-} = 1.72$
CN	−318.44273	$r_{Ar-C} = 1.42; r_{C-N} = 1.16$
SO_2H	−768.74388	$r_{Ar-S} = 1.82; r_{S-O} = 1.4308; r_{S-H} = 1.34;$ $\angle OSO = 119.32°; \angle CSH = 105°$
Cl	−681.89364	$r_{Ar-Cl} = 1.73$
Cl*	−681.95022	
F	−325.35101	$r_{Ar-F} = 1.35$
C≡CH	−302.61855	$r_{Ar-C} = 1.40; r_{C-C} = 1.19; r_{C-H} = 1.06$
$C_6H_5(\parallel)$	−454.64220	$r_{Ar-Ar} = 1.54$
$CH_3{}^{c,d}$	−266.47490	$r_{Ar-C} = 1.52; r_{C-H} = 1.09$
$CH_2F^{c,e}$	−363.91973	$r_{Ar-C} = 1.50; r_{C-H} = 1.09; r_{C-F} = 1.39$
$CHF_2{}^{c,d}$	−461.37973	$r_{Ar-C} = 1.50; r_{C-H} = 1.09; r_{C-F} = 1.36$
$CF_3{}^e$	−558.84589	$r_{Ar-C} = 1.48; r_{C-F} = 1.33°; \angle FCF = 110°$
$BH_2(\parallel)^b$	−252.84273	$r_{Ar-B} = 1.54; r_{B-H} = 1.16$
$BH_2(\perp)$	−252.83174	
$NH_2(\parallel)^b$	−282.20472	$r_{Ar-N} = 1.43; r_{N-H} = 1.0$
$NH_2(\perp)$	−282.18928	
$NH_3{}^{+c,d}$	−282.63215	$r_{Ar-N} = 1.5123$ (optimized); $r_{N-H} = 1.09$
$OH(\parallel)^c$	−301.72950	$r_{Ar-O} = 1.36; r_{O-H} = 0.96$
$OH(\perp)$	−301.72124	
H	−227.89130	$r_{Ar-H} = 1.083$

[a] Bond lengths are in ångströms; Ar refers to the benzene ring. [b] Trigonal bond angles are assumed. [c] Tetrahedral bond angles are assumed. [d] C–H bond is perpendicular to the plane of the benzene ring. [e] C–F bond is perpendicular to the plane of the benzene ring.

The molecular geometries were chosen to approximate experimentally determined values.[15] The benzenoid ring geometry was maintained constant for each substituent, r_{C-C} = 1.39 Å, r_{C-H} = 1.083 Å, and with all angles 120°. The geometries for the substituents are presented in Table I together with the total energies for the substituted benzenes. The chlorine substituent was calculated with (Cl*) and without (Cl) d functions.

Perturbations were induced by both positive and negative point charges. These charges were incorporated into the Hartree–Fock scheme by including these charged centers as nuclei without any basis functions assigned to them. The centers can have either a positive or negative charge associated with them. The HONDO program has been modified to allow such centers with either unit or fractional charges. Alternatively, the positive point charge may be approximated by assigning a very large scale factor (e.g., 50.0) to a hydrogen atom. This was the method used in the GAUSSIAN-70 series of programs. These perturbations were applied by positioning the unit charges 1 Å from the appropriate hydrogen atom along the C–H bond in either the meta or para position.

As a means of evaluating what effect a particular substituent has on the perturbed molecules, the following isodesmic reaction was used.



where X is the substituent and Y is the perturbing group in either the meta or para position. In an isodesmic reaction the formal bond types are conserved on both sides of the equation. This has the advantage that systematic errors inherent in minimum basis set calculations tend to cancel. The total change in energy ($\delta\Delta E$, eq 1) for the above reaction corresponds to a substituent effect for the perturbed system. This definition is consistent with the

$$\delta\Delta E = (E_C + E_D) - (E_A + E_B) = (E_D - E_A) - (E_B - E_C) = \Delta E_{subs} - \Delta E_H \quad (1)$$

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Table II. Energies of Perturbed Substituted Benzenes (au)

substituent	meta point charge +	para point charge +	meta point charge −	para point charge −
NO_2(∥)	−428.60476	−428.58124	−428.68115	−428.68378
NO_2(⊥)	−428.57348	−428.57315	−428.67296	−428.67361
dipole	−228.61981	−228.61924	−228.71913	−228.71979
CN	−318.45363	−318.45308	−318.54435	−318.54618
SO_2H	−768.75660	−768.75526	−768.84457	−768.84654
Cl	−681.90679	−681.90739	−681.99271	−681.99255
Cl*	−681.96537	−681.96598	−682.04751	−682.04749
F	−325.36951	−325.37161	−325.44328	−325.44149
C≡CH	−302.64000	−302.64015	−302.71068	−302.71203
C_6H_5(∥)	−454.66783	−454.66896	−454.73217	−454.73231
CH_3	−266.50046	−266.50150	−266.56128	−266.56063
CH_2F	−363.94149	−363.94167	−364.00989	−364.01013
CHF_2	−491.39945	−461.39941	−461.47185	−461.47229
CF_3	−558.86237	−558.86174	−558.94106	−558.94215
BH_2(∥)	−252.86519	−252.86279	−252.93279	−252.93685
BH_2(⊥)	−252.85647	−252.85775	−252.91919	−252.91815
NH_2(∥)	−282.23204	−282.23678	−282.28946	−282.28578
NH_2(⊥)	−282.21501	−282.21495	−282.27527	−282.27560
NH_3^+	--282.53680	−282.54261	−282.83803	−282.83261
unipole +			−228.11375	−228.10904
OH(∥)$_{syn}$	−301.75045	−301.75551	−301.81990	−301.81563
OH(∥)$_{anti}$	−301.75291	−301.75551	−301.81759	−301.81563
OH(⊥)	−301.74323	−301.74458	−301.81027	−301.80936
H	−227.91487	−227.91487	−227.97839	−227.97839

Table III. Isodesmic $\Delta\delta E$ of Reaction (kcal)

substituent	meta point charge +	para point charge +	meta point charge −	para point charge −
NO_2(∥)	10.58	11.46	−11.37	−13.02
NO_2(⊥)	10.92	11.13	−11.64	−12.04
dipole	11.35	11.70	−11.11	−11.52
CN	7.95	8.30	−9.11	−10.26
SO_2H	6.81	7.65	−8.52	−9.76
Cl	6.54	6.16	−7.51	−7.41
Cl*	5.28	4.90	−6.39	−6.38
F	3.18	1.86	−3.24	−2.12
C≡CH	1.33	1.24	−3.15	−4.00
C_6H_5(∥)	−1.29	−2.00	−1.80	−1.88
CH_3	−1.25	−1.90	0.46	0.86
CH_2F	1.14	1.02	−1.91	−2.07
CHF_2	2.42	2.44	−3.14	−3.42
CF_3	4.45	4.85	−5.06	−5.74
BH_2(∥)	0.70	2.20	−1.85	−4.40
BH_2(⊥)	−0.73	−1.53	−0.22	0.43
NH_2(∥)	−2.35	−5.33	1.48	3.79
NH_2(⊥)	−1.36	−1.32	0.70	0.49
NH_3^+	74.62	70.97	−74.53	−71.12
unipole +			−70.14	−67.18
OH(∥)$_{syn}$	1.64	−1.53	−2.07	0.61
OH(∥)$_{anti}$	0.10	−1.53	−0.62	0.61
OH(⊥)	0.99	0.14	−1.21	−0.64
H	0.00	0.00	0.00	0.00

usual definitions for linear free-energy relationships. Since the calculated energies are negative, a negative $\delta\Delta E$ corresponds to a substituent effect which is stabilizing (more favorable) compared to a hydrogen atom. Thus, the slope of any correlation between $\delta\Delta E$ and σ will be equal to the *negative* of the ρ value. This sign convention differs from that published previously.[5]

Results and Discussion

The total energies for the perturbed substituted benzenes are given in Table II. The isodesmic energy changes for the above reaction are given in Table III. Substituents with a π system that can either be orthogonal (⊥) or parallel (∥) to the π system of the benzene ring have been appropriately labeled. Since the meta positions for phenol with the hydrogen atom in the plane of the ring (∥) are nonequivalent, both were calculated. The configuration with the hydrogen atom on the same side as the point charge is labeled syn, and the other configuration is labeled anti. Their average value was used for comparisons.

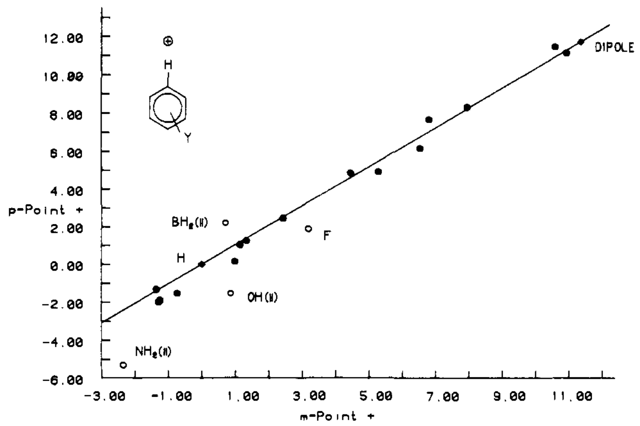

Figure 1. Plot of the isodesmic energy changes ($\delta\Delta E$) for the meta and para positive point charge perturbed substituted benzenes. The line drawn connects the points for hydrogen and the dipole "substituent" (diamonds) with a slope of 1.031. A regression line correlating all of the filled points has slope = 1.05 ± 0.02, $r = 0.997$.

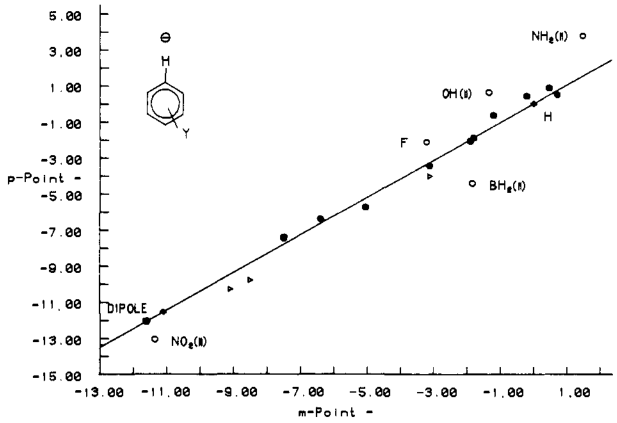

Figure 2. Plot of the isodesmic energy changes ($\delta\Delta E$) for the meta and para negative point charge perturbed substituted benzenes. The line drawn connects the points for hydrogen and the dipole "substitutent" (diamonds) with a slope of 1.037. A regression line correlating all of the filled points has slope = 1.05 ± 0.2, $r = 0.997$.

Figure 1 shows the correlation between meta and para positive point charge perturbed substituted benzenes. Figure 2 is a similar correlation using a negative point charge. The lines shown have been drawn through the points for hydrogen and the dipole "substituent". Since the dipole (3.5 D, the experimentally determined moment for nitromethane) is a pure "field effect" substituent, the substituents which are not on the line must have additional effects operating. Any mesomeric contribution to the substituent effect can be seen as an enhanced para effect. Thus, points above the line correspond to π-destabilizing groups while points below the line correspond to π-stabilizing groups.

For the positive point charge perturbation (Figure 1), four points (open circles) are clearly off the line. Of these, the amino, hydroxy, and fluoro groups are strong π donors; the boro group is a strong π acceptor. This mesomeric effect cannot be due to direct resonance interaction with the perturbing site because such interaction is not possible in this system. The mesomeric contribution must stem from a strong interaction between the π system of the benzene ring and suitable orbitals on the substituent. When these groups are rotated to their orthogonal (⊥) conformation, such that π conjugation is reduced or eliminated, the corresponding points are much closer to the line. It is important to note the absence of significant mesomeric destabilization by the cyano, nitro, sulfonyl and trifluoromethyl groups.

For the negative point charge perturbation (Figure 2), five points (open circles) are clearly off the line and several points are borderline cases (triangles). Again, the fluoro, amino, boro, and hydroxy groups show mesomeric interaction, but now the nitro group shows significant mesomeric stabilization. The cyano and

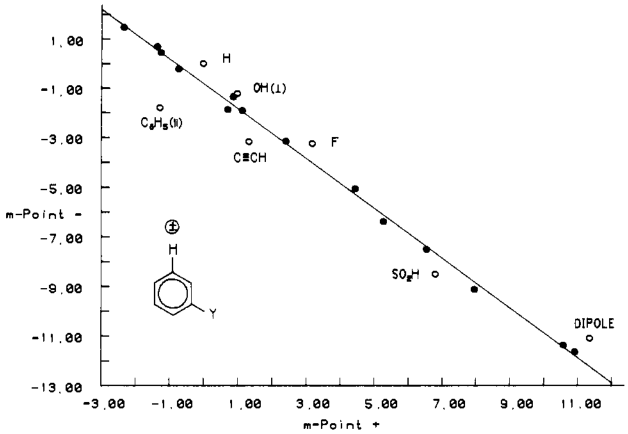

Figure 3. Plot of the isodesmic energy changes ($\delta\Delta E$) for the meta point charge perturbed subsituted benzenes. The regression line shown correlates the filled circles with slope = −1.01 ± 0.02, r = 0.999.

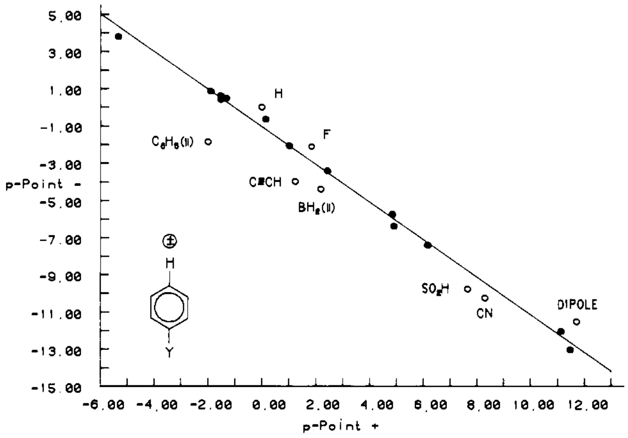

Figure 4. Plot of the isodesmic energy changes ($\delta\Delta E$) for the para point charge perturbed substituted benzenes. The regression line shown correlates the filled circles with slope = −1.01 ± 0.03, r = 0.998.

sulfonyl groups are somewhat below the line and indicate some mesomeric stabilization. As in the positive point charge perturbed system, rotation of the groups to their orthogonal conformation decreases their resonance interaction. Notice that the phenyl substituent does not interact mesomerically.

The slopes for the two lines are slightly greater than unity (1.034 ± 0.004). This effect may be attributed to the effective dielectric properties of the benzene ring. Though the magnitude is smaller, the direction is the same as that found by Exner[10] (1.14 ± 0.03) for the ratio of para to meta substitutent constants. Interestingly, if one correlates the substituents without lone-pair electrons as recommended by Exner, one obtains an excellent correlation (r = 0.999 Å) with a slope of 1.15 ± 0.02, identical with his correlation within experimental error.

One of the original assumptions for the Hammett equation was that the substituent constants are independent of the nature of the reaction and that different charged reaction centers will only change the sign of the reaction constant. If this is strictly true, then a plot of substituted benzenes perturbed by a positive charge vs. those perturbed by a negative charge should give a straight line with unit slope. Figure 3 shows such a plot for the meta perturbed molecules. The para perturbed set is shown in Figure 4.

The observed scatter in these plots shows that the substituent effects are not totally independent of charge type. A useful analysis is provided by dissecting the substituent effects into dipolar and polarizability components. The dipolar component has a purely reciprocal effect toward negative and positive charges; the *polarizability component is stabilizing toward both charges.* Substituents generally fall below the line connecting hydrogen and the pure dipole "substituent". The degree of deviation below the line is a measure of substituent polarizability relative to the hydrogen and pure dipole standards. An important result of this analysis is that many substituents (solid circles) form an empirical linear correlation of their own. These substituents have essentially the same polarizability effect and constitute many of the common substituents used in Hammett-type correlations. That is, σp correlations determined from such substituents alone may be expected to give accurate linear relations independent of reaction charge type. In comparison to this group of substituents, the hydrogen and fluoro group are significantly less polarizable. This property undoubtedly accounts for the anomolous behavior frequently observed for these substituents.[16]

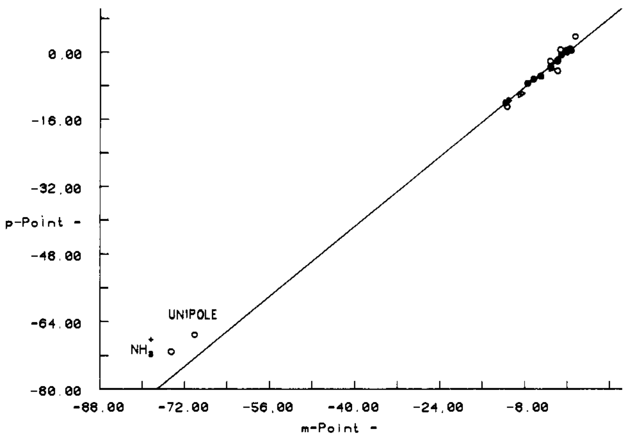

Figure 5. Plot of the isodesmic energy changes ($\delta\Delta$E) for the meta and para negative point charge perturbed substituted benzenes. The line drawn connects the hydrogen and the dipole "substituent" as in Figure 2 and has been extended to include the ammonium group and the unipole "substituent".

The phenyl, ethynyl, sulfonyl, and (in the para case) cyano groups display greater polarizability than "standard" substituents. Hence, their experimentally determined substituent constants will be highly dependent on the reaction type. Indeed, this has been observed. A recent compilation of substituent constants[17] shows for the phenyl group an average σ_m = 0.04 ± 0.14 and σ_p = 0.05 ± 0.10. Recently, unexpected stabilization of a carbonium ion α to a cyano group was reported.[18] This stabilization is consistent with a dominating polarizability effect. Taft et al.[19] have also recently called attention to the effects of differing substituent polarizability, particularly in comparing solution and gas-phase systems.

The magnitude of the polarizability effect is several tenths of a kilocalorie per mole. It is instructive to show that this magnitude is consistent with a classical charge-induced dipole polarization. The electrostatic energy is given by eq 2 for the polarizability α, charge q, and macroscopic dielectric constant D. An electronic

$$E = -\alpha q^2/2Dr^4 \qquad (2)$$

charge in a vacuum 5 Å from a polarizable unit having a typical longitudinal bond polarizability value,[20] $\alpha = 30 \times 10^{-25}$ cm^3, thus produces a classical polarization energy of 0.8 kcal mol^{-1}, a value of the correct order of magnitude to account for the results.

Charged substituents, like the ammonium group, have been a point of contention for some time. The assumption has been made that the trimethylammonium group has no resonance effect and, therefore, can be used to separate field and resonance effects.[21]

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Alternatively, a significant resonance electron-donor effect has been claimed for both ammonium and substituted ammonium groups.[22] Doubt has also been expressed as to whether dipolar substituents should be mixed with unipolar substituents because of the difference in angular dependence of Coulombic effects.[2] To help solve this problem, the point charge perturbed anilinium ion can be included in plots of the types shown in Figures 1 and 2. Figure 5 is an example using a negative point charge perturbation. Clearly the point is above the line indicating a mesomeric effect in addition to any inductive effects. However, when a pure positive point charge is used to model a unipolar substituent, it too is above the line drawn between the hydrogen and pure dipolar "substituent". It is impossible for the pure point charge to donate electrons in a mesomeric sense in this system. The apparent effect of a unipolar group is an interaction with the ring in such a way as to mimic a resonance effect. If one draws a line between hydrogen and the pure unipolar "substituent", the point for the ammonium group falls on the line. The slope of the line is slightly less than unity (0.96 ± 0.00) which is to be expected since there is no angular dependence for the Coulombic interaction between unipoles and the meta position is closer than the para position.

If the ammonium group is included in Figure 3 or 4, it falls on the correlation line. Therefore, the polarizability of this substituent is similar to most of the other substituents.

Correlations between the isodesmic energy changes and various linear free-energy relationships are, in general, predictable. Substituent scales which minimize resonance effects show the best correlations. This is the case for single- and dual-parameter equations. It is interesting to compare the correlations obtained here with Yukawa's σ^0 values and Wepster's σ^n values. Both authors claim to have removed through-bond resonance effects. Since through-bond resonance is impossible for the point charge perturbed substituted benzenes, correlations using the Yukawa–Tsuno equation should give an $r^\pm$ value (resonance parameter) of zero if through-bond resonance has been eliminated.

For the positive point charge perturbed system, correlation with σ^0 values gives $r^+ = -0.11$ ($r = 0.973$), whereas σ^n values give $r^+ = 0.03$ ($r = 0.970$). For the negative point charge perturbed system, σ^0 values give $r^- = 0.27$ Å ($r = 0.967$ Å) and σ^n values give $r^- = 0.03$ Å ($r = 0.980$ Å). For both sets of perturbations, single-parameter correlations using σ^n values are better than the corresponding σ^0 values. The results show that σ^0 values still contain some through-bond resonance effects, whereas the σ^n values apparently do not.

Conclusions

1. The original assumption that substituent effects are independent of reaction type is valid for most substituents, including methyl, trifluoromethyl, chloro, amino, ammonium, nitro, and hydroxy groups. Highly polarizable groups such as phenyl, ethynyl, sulfonyl, and (in the para position) cyano and weakly polarizable groups such as hydrogen and fluoro must be treated with care. Such groups should *not* be included in Hammett correlations on the same basis as "normal" substituents.

2. A single resonance parameter scale is not attainable. This is due to a lack of resonance destabilization for nitro, cyano, and sulfonyl groups with positively charged probes. For negatively charged probes, these groups are mesomerically active. Dual substituent parameters should be modified to reflect this difference[8,10] (e.g., $\sigma_{R^+} = 0.0$ for NO_2 and CN).

3. Unipoles show apparent interaction with the benzene ring and appear as strong π donors even though mesomeric interactions are minimal.

4. There is a slightly larger inductive effect at the para position than at the meta position. The effect is so small, however, that corrections of σ_I values are not warranted.

5. Weptster's σ^n values[9] are the best set of "normal" substituent constants and are recommended for correlations using the Yukawa–Tsuno equation.

6. The phenyl ring stabilizes both a positive and negative reaction center. Mesomeric interactions between the two π systems are minimal and the stabilization is undoubtedly due to the polarizability of the benzene ring.

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