On the Separability of Inductive and Resonance Effects
within the Framework of Linear Free Energy Relationships¹

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Abstract

A continuation of non-linear least-squares analysis of aromatic reactivity data is discussed. More general forms of the dual substituent linear free energy equation reveal Taft's assumption of proportional sensitivity of $\log k/k_0$ to inductive and resonance effects is reasonable, at least for σ^0 - and σ -type reactivities. However, various transformations among parameter sets are shown to hold which imply I and R effects are not uniquely separable by statistics, without specification of the magnitude of the sensitivity proportionality constant. Relations of the latter to such questions as positional dependence of I and R effects are discussed. Models for the total I-effect which include classical and π -inductive effects are presented and analyzed relative to each other and in relation to accompanying resonance effects.

Introduction

A program for a priori statistical refitting of aromatic reactivity data to the Taft linear free energy relationship has recently been outlined.² The principal purpose for reexamination of this relationship, generally expressible as $\log k/k_0 = I + R$, was to determine what physical significance attaches to imposition of the constraints which transform it to its operational forms,³

$$\begin{aligned}\log k^p/k_0 &= \rho_I \sigma_I + R^p \equiv \rho_I (\sigma_I + \sigma_R) \\ \log k^m/k_0 &= \rho_I \sigma_I + R^m \equiv \rho_I (\sigma_I + \alpha \sigma_R)\end{aligned}\quad (1)$$

The corollary question of what, if anything, is accomplished by relaxation or modification of these constraints was also considered. Accomplishment, in the latter sense, has implications both to the understanding of divisions of total observable substituent effects, if possible in terms of physically justifiable reaction system models, as well as to improvement of statistical fitting. In the present discussion, concern with correlational improvement will be limited to questions of divisibility of effects and of applicability of such models, and not directly to how the correlations may be improved for their own sakes.

The completely general dual substituent equation,

$$\log k/k_0 = \rho_I \sigma_I + \rho_R \sigma_R \quad (2)$$

may be mathematically constrained in a variety of ways to conform to models of physical reality. In Appendix A it is shown that at least four independent constraints are required to yield unique solutions in a mathematical sense if ρ_I, ρ_R, σ_I and σ_R are independent variables. Taft's equations 1 arise from

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more stringent constraints than minimally required, *i.e.*, he takes $\rho_I^P = \rho_I^m$, $\alpha \rho_R^P = \rho_R^m$ and a standard reaction (benzoic acid ionizations in H_2O at 25°) for which $\rho_I \equiv 1.000$ are three plus the additional specification that $\rho_I = \rho_R$. The latter condition removes one independent set of variables.

Several important physical demands attend imposition of these constraints. Independent of reaction, effects,

1. there is a constant ratio of sensitivity to inductive and resonance/ and independent of reaction and substituent,
2. inductive effects are the same from the m- and p-positions,
3. there is a constant ratio of resonance effects from the m- and p- positions.

Of these, 3. is known to be unrealistic, although within general groupings where valence-bond-represented conjugation between the substituent and reaction center is or is not possible, some correlation is noted. For the former, α 's from 1/5 to 1/10 pertain, for the latter, 1/2 to 1/3. As for 1. and 2., these are suspect; 2. has had some examination, but only in a limited manner and under conditions which imply 1.³ If 1. and 2. are ~~not~~ physically realistic, relaxation of the constraints which imply them should not substantially improve the statistics for fitting the reactivity data to which they pertain. If they are not, their interactions with each other and with 3. are crucial. The bearing of all three upon such questions as the mechanism of transmission of the I-effect in aromatic versus aliphatic systems, the related proportionality of σ_I and σ^* , and upon the overriding question of whether I and R can be satisfactorily separated at all, are the paramount physical issues of the investigation.

Here we constrain by requiring $\rho_I^P = K_I \rho_I^m$, $\rho_R^P = K_R \rho_R^m$, by defining a standard reaction and by holding at least one σ -value. The standard reaction is the same as Taft's if it is in the group of reactions considered; with σ_R for one substituent held, the minimum constraint conditions are met (see Appendix A). The correlation equations employed are then,

$$\begin{aligned} \log k^P/k_0 &= K_I \rho_I \sigma_I + K_R \rho_R \sigma_R \\ \log k^m/k_0 &= \rho_I \sigma_I + \rho_R \sigma_R \end{aligned} \quad (3)$$

with all parameters assumed independent and with the σ 's solely functions of substituent and not of position. Of the former physical conditions, 3. remains, 2. is weakened to read, ... proportional ... rather than the same, and 1. is removed.

These appear physically more consistent under the presumptions that substituent and reaction center effects are truly separable, and, also, that a given substituent may contribute different proportions of its total effect to I and R for different reactions. The notion of separability conforms to the assignment of a single σ_I and σ_R dependent only upon the nature of the substituent, and a single ρ_I and ρ_R for a given reaction group, which determines ρ_I/ρ_R , with modification due to geometry (position) reflected in K_I and K_R . It should, of course, be noted that the greater flexibility of the present equations is accompanied by computational complexity; this is, however, surmountable by use of non-linear statistical analysis procedures programmed for digital computer handling.

The statistical procedures employed have been outlined in ref. 2 and discussed in more detail in section V of ref. 4. A modification of the program was made part way through the present work to more efficiently utilize computer storage. Rather than simultaneous optimization of all parameters by the Gauss-Newton procedure,⁵ the so-called block-diagonal modification was employed which varies groups of parameters in consecutive fashion.⁶ The general order of variation was, upon input of guesses for the σ 's and K's, to determine best ρ 's (by least-squares). Using the latter and the K's, best σ 's were generated followed by determination of the K's from the first order ρ 's and σ 's. This process was continued cyclically until either all ρ and σ have converged within prespecified limits (0.005) or the precision of fit to the data no longer changes upon cycling (threshold of 0.05% of the standard deviation). In all cases tested, where initial guesses were sufficiently good to provide monotonic convergence by the original method, the converged results of the block-diagonal method were found to agree with the latter.

Again, as in ref. 2, the groups, OCH₃, CH₃, F, Cl and NO₂ (hydroxylic medium) were chosen as test substituents. The choice of these groups was manifoldly motivated: they appear from other correlations to be the least sensitive to specific effects such as solvation, and, at the same time, they have been sufficiently widely employed so as to contribute significantly to, if not to essentially determine the correlations of all aromatic reaction series studied to date. As well, a wide range of electron donor-acceptor capacity is covered by these substituents, both in the inductive and resonance effect sense.

A total of 17 σ° - and 24 "benzoic-type," hereafter called σ -type or simply σ -, reactivities have been examined, both within these groupings and together. For the former and latter sets, 120 and 211 individual log k/k₀ data respectively were available. These comprise ~70% and ~90% of all possible data for the reactions and substituents considered and yield average data-per-parameter ratios of ~3 and 3.8 for the σ° - and σ -type reactivities.⁷

Results and Discussion

A. Statistics for σ° - and σ -Reactivities

As indicated in the Introduction, interpretation of the separated I- and R-effects by the Taft equation must be accompanied by justification of the physical constraints by which the separation is effected, and hopefully also by statistical evidence to assure that the separation is unique. In extending previously described work,² several results suggesting the Taft equation is generally valid were obtained but some disquieting and incompletely understood features were also uncovered.

Incorporation of 5 new σ° -reactivities (13-17 in Appendix B) into the previously examined set indicate the best K_I and K_R to be 0.95 ± 0.01 and 1.97 ± 0.03 independent of initial input K's with σ_I held at Taft's values.⁸ Here and elsewhere, the initial choices for σ_R are Taft's σ_R° values. These results agree with those obtained on the smaller σ° -set: the standard deviation of fitting (SD) is improved by inclusion of these reactions from 0.031 to 0.029. Fitting of the σ -type and σ° -type sets

Table I

Initial and Optimized K_I and K_R Values for σ° -Reactivities
under Minimum Constraint

		Optimized K_I, K_R [10^2 SD]			
Initial K_I	K_R	1.8	2.0	2.3	3.0
0.75	---		0.88, 2.25 [2.85]	0.88, 2.53 [2.83]	0.85, 3.19 [2.95]
1.00	---		0.99, 2.04 [2.84]	---	0.99, 2.92 [2.75]
1.15	1.06, 1.78 [2.93]		1.06, 1.94 [2.88]	1.06, 2.19 [2.81]	---
1.30	1.14, 1.70 [3.09]		1.14, 1.86 [3.04]	1.14, 2.09 [2.97]	1.13, 2.66 [2.81]

Table II

σ° -Values for Converged Sets with Different K_I and K_R Values

		Substituents				
$K_I =$	$K_R =$	OCH ₃	CH ₃ ^a	F	Cl	NO ₂
0.88	2.53	0.20, -0.34		0.42, -0.23	0.43, -0.13	0.64, 0.28
0.99	2.04	.28, -.44		.51, -.36	.51, -.26	.68, .17
1.14	2.09	.32, -.47		.59, -.46	.61, -.39	.86, -.10
Taft's σ -values		0.26, -0.42	-0.05, -0.10	0.52, -0.33	0.46, -0.19	0.63, 0.18

^a Both σ_I and σ_R held at Taft's values, the former only for convenience. When allowed to go free, $0.00 > \sigma_I > -0.08$ with insignificant effects on precision of fit.

together under similar conditions yielded essentially the same K_I results but $K_R \sim 2.2$. The SD's for both sets were 0.038-0.039. These results are taken to suggest that distinctions drawn between reactivities wherein the reaction group can and cannot conjugate with the aromatic framework is useful in the sense of precision of fit but less so in terms of K_R (or α). Intuitively-directed inclusion of the 5 new reactivities into the σ^o -set significantly changed none of the results previously obtained for this set, e.g., K_I and K_R values were 0.97 and 1.9.² At the same time, the σ^o -reactivities are found to correlate with eq. 3 significantly better than do the σ -type although both fit within precisions expected if the experimental data contain on the average 5% uncertainty per measured point. With reference to distinctions between the σ^o - and σ -reactivities on the basis of K_R , the optimum value for this parameter is found to agree with Taft's assignment for the σ^o -set ($\alpha = 1/2$), but for the σ -set, the value of 2.2 for K_R is somewhat better, if anything, than 3.0 (Taft's 1/3) for which SD = 0.043. It is likewise pertinent to note that although K_I is found to be somewhat smaller than unity, this is probably not significant, contrary to a suggestion in ref. 2. Maintaining $K_I = 1.00$, the SD's of fit for the σ^o -, σ - and σ^o - plus σ - sets are 0.030, 0.039 and 0.039.

When fitting is attempted holding only to the minimum constraint set, with $\sigma_R(\text{CH}_3) = -0.10$, a broad range of equally good fitting K_I and K_R values are obtained. Over the range of initial K_I employed above and the extended K_R range down to 1.8, a variety of parameter sets were evolved all of which fit the σ^o -set to SD's of 0.028-0.030. Table I presents some of these results in terms of initial and optimized K-values. The final K_I 's are seen to span the range 0.85 to 1.15 and are generally coupled so that small K_I values accompany large K_R 's. The various optimized ρ and σ sets are quite different between sets, cf., Table II where this is illustrated in terms of the σ 's. Similar multiple optima results are obtained for the σ - and mixed sets. Here the SD's are 0.034 ± 0.002 as long as the initial K_I is unity or less: for larger K_I , convergence is to SD ≈ 0.040 . In contrast, a test case where $\log k/k_0$ values were constructed from hypothetical ρ and σ values, this statistical method was able to effectively reproduce the parameters, even to the extent where the data are invested with up to 3% random errors.

It is apparent from these results that equations 3, when minimally constrained (in a mathematical sense) cannot produce a unique parameter set for the reactivity series considered. This may be due to one, or both, of two fundamentally different reasons. The first is concerned with the freedom allowed in equations 3, i.e., that all the parameter independence assumed does not exist. The second involves the interplay of data error and degree of correlation between various parameters, and is purely a statistical problem where the first is physical-statistical. If I and R are in some way dependent, there clearly will be more than one way equation 3 can fit the data: if data errors are significant and trends in $\log k/k_0$ associated with change in one parameter are producible in part by another, or others in concert, multiple solutions are likewise possible.

Partial resolution of this question is forthcoming from the following observations. When the last statistical analysis is repeated holding K_I constant at unity and also at 0.87, optimized parameter sets which vary with initial choice of K_R but which yield essentially identical fitting are again obtained. The choice of 0.87 as one fixed value for K_I is connected with analysis on the I-effect discussed below; the results obtained with this value

are identical for present purposes with those obtained using K_I of unity. Upon initial choice of 2.0, 2.5 and 3.0 for K_R , with $K_I = 0.87$, converged values for the former of 2.02, 2.47 and 2.92 were obtained with corresponding SD values of 0.0295, 0.0288 and 0.0285 for the σ^0 -set. The same results are obtained for the σ^- and mixed reactivity sets. While the fit is independent of K_R , the converged σ 's and ρ_R^m 's are not. The former quite precisely follow the relationship, $\sigma_I + \sigma_R = \text{constant}$ (f (substituent)) among the various converged sets, while the latter change proportionally among these sets. Minor variations are noted among the other ρ 's: the overall effect appears to be one where parts of I and R are shifted into each other, both for different K_R solutions at constant K_I and among the different K_I solutions.

Examination of the constraint equations in Appendix A-2 shows the two observations, i.e., on $\sigma_I + \sigma_R$ and on ρ_R^m , to be consistent as long as ρ_R^P / ρ_I^P is essentially constant over all reactions and near unity if there is no change in any ρ 's but ρ_R^m . Table III shows the constancy of $\sigma_I + \sigma_R$ among the various solutions for the σ^0 -set. The ratio of ρ_R^P / ρ_I^P is unity with apparently unimportant deviations, e.g., for $K_I = 0.87$, $K_R = 2.02$, this ratio is 1.041 ± 0.095 , with $K_R = 2.92$ the ratio is 1.050 ± 0.116 . In Table IV some reactions chosen randomly from the σ^0 -set illustrate the shifting under change of K_I between I and R.⁹ This shifting, it should be pointed out, leaves the total predicted effect, $\log k/k_0$, unchanged not only in the statistical sense (SD for all reactions) but, because of the extra freedom introduced by the ρ_R^P , ρ_I^P dependency, in the individual points as well.

We are led therefore to conclude that Taft's assumption of proportional sensitivity to inductive and resonance effects is correct, at least for the reactions thus far considered. Whether this formalism may be carried over to the reactivities where direct conjugation is possible between substituent and reaction center is not presently known. It is not unreasonable to speculate, however, that if it does hold, at least a different (larger) constant for ρ_R^P / ρ_I^P will pertain. Some of the present difficulties in defining a single σ_R for a substituent may be overcome by this expedient. Work is presently underway to see if modification of the constant is sufficient to improve correlation or whether this constraint must be entirely removed for σ^+ and σ^- reactivities.

B. Interaction Modes and Models for the I-Effect

From the results of Table III it is apparent that σ_I sets may be derived which fit the data satisfactorily, but which are not proportional to Taft's σ_I set and thereby are not proportional to σ^* . Again, from Appendix A-2, where K_I is held and σ_I is a set equal or proportional to Taft's, there are primed sets where,

$$\sigma_I' = \sigma_I - \frac{K_I \left(1 - \frac{K_R}{K_R'} \right)}{K_R' - K_I} \sigma_R \quad (4)$$

Therefore, unless σ_I and σ_R are proportional, σ_I' is not proportional to σ^* . This result raises several interesting questions; i.e., why should σ_I for aromatic reactivities and σ^* for aliphatic and alicyclic reactivities be proportional, what contributes to σ_I above and beyond the factors determining σ^* , and are these effects separable. Further, are the latter clearly associated

Table III

 σ^o -Values for Sets with K_I held at 0.87 and 1.00 with Various K_R

Substituent	σ_I σ_R					
	$K_I = 1.00$			$K_I = 0.87$		
	$K_R = 2.02$	2.94	3.88	$K_R = 2.02$	2.47	2.92
OCH ₃	0.279 -.422	0.178 -.313	0.142 -.278	0.246 -.382	0.197 -.330	0.168 -.302
CH ₃	-.050 -.076	-.082	-.086	-.083	-.086	-.090
F	.514 -.362	.428 -.269	.397 -.238	.456 -.265	.421 -.227	.402 -.207
Cl	.506 -.253	.444 -.187	.422 -.165	.442 -.149	.422 -.127	.410 -.116
NO ₂	.668 .147	.704 .108	.717 .095	.578 .314	.620 .269	.644 .245

Table IV

Shifts Between I and R upon Change of K_I^a

Reaction, ^b	Substs.	I^m, R^m	
		$K_I = 1.00$	$K_I = 0.87$
2	OCH ₃	0.134, -0.094	0.122, -0.081
	F	.247, -.080	.227, -.056
	NO ₂	.321, .033	.288, .066
4	OCH ₃	.300, -.231	.271, -.198
	F	.553, -.198	.502, -.137
	NO ₂	.719, .080	.637, .163
16	OCH ₃	-.185, .171	-.160, .147
	F	-.341, .147	-.296, .102
	NO ₂	-.444, -.060	-.376, -.121

^a K_R (SD) for both sets of 2.02 (0.0290 ± 0.0006); I^P obtainable from $K_I I^m$, R^P from $K_R R^m$.

^b Reactions numbered as in Appendix B.

with the π -electrons of the framework and, if so, how are they related to the conjugative effects presumably responsible for σ_R .

Two major effects are generally supposed to characterize induction in aromatic systems. The first, also present in saturated molecules, is the classical inductive effect which may be due either to electrostatic interaction through space of the substituent X and the reaction center Y, or to transmission via the framework σ -bonds with damping, or more likely by both, if, in fact, the distinction is meaningful.⁴ If simple models pertain, the effect in this mode of a substituent in the m-position should be greater than in the p-position.¹⁰ The inductive capacity of a substituent will also polarize the π -framework in aromatic molecules, principally through polarization of the framework atom to which it is attached. This is the π -inductive effect, variously called the inductoelectromeric¹¹ and non-classical inductive effect,¹² which is expected by qualitative valence-bond and intuitive notions to be larger from the p- than the m-position. The two effects, then, operationally inseparable, in contrast to separations of I- and R- by such expedients as twisting of the substituent relative to the ring framework,¹³ may yield total inductive effects of equal magnitude from the m- and p-position, but can only in total be proportional to the effects in aliphatic systems if they are proportional to each other! This proportionality has been assumed by various workers without much justification¹⁴; it is possible, however, to semi-quantitatively indicate where it may be expected to hold.

Taking the monopole or dipole moment charge induced by X at the ring site of attachment equal to e_{RX} , the electrostatic energy is given as,

$$E_{El} = \frac{e_Y e_{RX}}{Dr} \quad \text{or} \quad \frac{e_Y \mu_{RX} \cos \theta}{Dr^2} \quad (5)$$

where D is the averaged dielectric for the medium between sites RX and Y, r is the distance between these sites, μ_{RX} is the dipole moment of the ϕX dipole considered to be located at the ring site of attachment and θ is the angle between the dipole direction of ϕX and the line joining sites RX and Y. If through-the-bonds transmission also enters, e_{RX} and e_Y are damped upon progression along the framework by a factor ϵ per bond, as is usually assumed, and if the interactions from these perturbed ring sites is also electrostatic, the total classical induction energy is,

$$E_{CI} = \frac{e_Y e_{RX}}{D} \left[\frac{1}{r} + \epsilon \sum \frac{1}{r'} + \epsilon^2 \sum \frac{1}{r''} \dots \right] \quad (6)$$

Here the sums are over all interaction configurations arising from the bond transmission models, where the number of primes indicates the number of bond dampings for Y and RX in total. D is assumed the same for all paths and ϵ the same independent of the nature of the bond.¹⁵

The π -inductive effect, on the other hand, arises from the perturbation at RX of the π -orbital at this site followed by resonance distribution to the rest of the π -framework. This effect at RX is reasonably $C e_{RX}$, where C is the coupling factor relating the perturbation of all AO's at this site to the π -AO of proper symmetry.

We may therefore picture the entire inductive effect as,

$$E_I = \text{electrostatic} + \text{through-the-bonds} + \pi\text{-inductive}$$

$$= f(r, e_{RX}, e_Y; p, \epsilon) + f(\pi\text{-framework}, e_{RX}, e_Y \text{ or } e_{RY})$$

where r , e_{RX} , e_Y and ϵ are as previously defined, p expresses the number of paths and bonds for the framework induction mode and e_Y or e_{RY} allows for the cases of conjugating and non-conjugating reaction centers. Specifically, as derived in footnote 15 and in ref. 4, section IV, respectively, for m - and p -disubstituted benzenes,

$$E_{CI} = \frac{e_Y e_{RX}}{Dr} (1 + 3.85\epsilon) \quad (7)$$

$$E_{\pi I} = A_I \bar{\nabla}^X \bar{\Delta}^Y \quad (8)$$

Here, $\bar{\nabla}^X = 2 \delta_{RX}$, $\bar{\Delta}^Y = \delta_{RY'} - \delta_{RY}$ (for non-conjugating Y) and A_I is a function of the framework and positions of substitution.¹⁹ For example, for the σ^o -reactivities (non-conjugating Y),

where the standard substituent, X_o , is taken as sp^2CH_2 as in ref. 4, our interest is in the following models for the π -inductive effect.

For these models, $A_{I \text{ meta}} = -6.9 \times 10^{-3}$ and $A_{I \text{ para}} = -14.4 \times 10^{-3}$, as obtained by first and second order perturbation theory with self-consistent charge redistribution effects considered.²⁰

Upon reexamination of the assumptions leading to these results, both the classical and π -inductive effects may be shown to be similarly dependent upon coulomb integral properties of X, X_o , Y and Y', much in the manner previously demonstrated for resonance effects,⁴ and thereby to be simple combinable.

$$\Delta E (\text{Total Induction}) = \left[\frac{1 + 3.85\epsilon}{2L_Y L_X Dr} + A_I \right] \bar{\nabla}^X \bar{\Delta}^Y, \quad (9)$$

under the following assumptions.

a) The charge at the ring site of attachment of Y may be related to the effective charge of Y by $e_{RY} = \epsilon(e_Y - e_R)$, where e_R represents the unperturbed charge at this ring site and ϵ is invariant to the nature of Y. This often made assumption has been previously employed in the combination of electrostatic and through-the-bonds models¹⁵; some recent as well as long standing observations relating electronegativities of atoms and the bonds formed between them,²¹ especially for grossly different X's and Y's, suggests, however, that this may be less secure an approximation than desired.

b) The effective coulomb integral for the π -AO at the substituted ring site can be coupled proportionately to the perturbation experienced in the σ -orbital at this site due to substitution. If $e_{RY}^{\pi} = C e_{RY}^{\sigma + \pi}$ and $e_{RX}^{\pi} = C e_{RX}^{\sigma + \pi}$, then by the familiar linear relationship between coulomb integral and charge density, i.e., $\delta = \omega \beta(q_0 - q)$,

$$\delta_{RY} = \omega \beta(1 - C\epsilon)(e_Y - e_R) \quad (10)$$

Therefore, $L_Y = -\omega \beta C \epsilon$ and $L_X = -\omega \beta C$, as used in equation 9 and,

$$\begin{aligned} \overline{\Delta}^Y &= 2L_Y (e_{Y'} - e_Y) \\ \overline{\nabla}^X &= L_X (e_{RX} - e_{RX_0}) = L_X \epsilon (e_X - e_{X_0}) \end{aligned} \quad (11)$$

In the event these assumptions hold, the inductive effects in aromatic systems will understandably be proportional to those noted in aliphatic systems where π -induction is not possible. All else being equal, enhancement due to the latter effect would be $(A_I + B)/B$, where B is the classical effect: other changes, e.g., in geometry may, of course, introduce further proportionality factors.

Order of magnitude estimations of the contributions of the classical and π -inductive effects may be made as follows. With $\epsilon = 1/10$ ²² and C taken as unity (equal sensitivity of σ - and π -AO's to inductive perturbation) leaves only ω for determination of the L-parameters. The proportionality constant relating the coulomb integral and charge density changes should be somewhere between the values used for the framework considered as a whole, where distant electron repulsion effects are averaged in ($\omega = 1.2-1.4$),²³ and that for the carbon atom in isolation ($\omega = 4.6$).²⁴ This argument is based on the understanding that we are here considering C-X (or C-Y) fragments, where some effect of X (or Y) upon carbon is expected: the value, $\omega = 3$, roughly the average of extremes, is employed.

Therefore, taking the effective electronic charge as 1×10^{-10} esu, following Ketelaar²⁵ and $D = 2.0$,⁴ the classical term coefficient of equation 9 is roughly -0.10 for m-position cases and -0.087 for p-position cases. These values are for the energy in units of β ($\sim -2_+$ ev); the negative signs of the coefficients reflect the increase in energy for $(\delta_{RY'} - \delta_{RY})$ and $(\delta_{RX} - \delta_{RX_0})$ of the same sign. Addition of the π -inductive effects as expressed in A_I raises the ratio of the total effect to near unity, i.e., $p/m = -0.103/-0.107$.

What seems especially significant, then, is that the direct or classical inductive effects are formally and physically inseparable from the π -inductive effects which they, in a sense, produce, not only for

a given substituent but over all substituents. The principal physical manifestation of the mixing is to make the total effects about the same from the m- and p-positions.²⁶

C. Theory of Differences Between I and R

Equation 9 which relates the total inductive effect to coulomb integral differences at the ring sites of attachment of X and Y is similar in form to equations developed in ref. 4 for resonance effects. There is however a strong operational difference between these equations which resides in the origin of the coulomb integrals considered!

In the resonance term, δ_X and δ_Y refer to the coulomb integrals for the π -electrons in the π -orbitals of X and Y which can conjugate with the framework. The π -inductive effect on the other hand, and hence the total inductive effect by the relationships here developed, depends upon the change ~~in the exchange~~ in coulomb integrals induced at the ring site by inductive feeding or withdrawal by X and Y, i.e., δ_{RX} and δ_{RY} are inductively caused perturbations due to X and Y. These deltas, and as a result ∇^X (resonance) and $\bar{\nabla}^X$ (induction), are not necessarily the same, nor even necessarily simply proportional. They may in fact be of opposite sign.

It is well established in heteronuclear diatomic molecule theory that σ -bonds may be polarized differently than π -bonds in the same molecule, i.e., in the molecule AB, as an extreme case, A may appear electronegative with respect to B as regards charge density distributions in the σ -MO's while appearing electropositive in the π -MO's.²⁷ In the systems of present concern this conceptual difference is reflected in qualitative thinking about various substituents, e.g., methoxy while being a good electron withdrawer inductively is a donor by resonance; the nitro group, in contrast, withdraws by both modes. Valence bond structures such as $F \leftarrow C \leq$ and $F^+ = C \leq \ominus$ have similar implications as of course do σ_I and σ_R for a given substituent when these parameters are of different sign.

This is of course not to imply that interactions in the different MO (symmetry) dimensions are not related. In truth they must be, albeit not simply: here, whatever relationship there is may be additionally clouded by the models chosen. Substituent groups in many cases are unrealistically viewed as quasi-atoms, e.g., NO₂. When comparisons are drawn between substituents where the quasi-atom is a more sensible model, some of the apparent incoherence disappears, e.g., among the isoelectronic groups, F, OH, NH₂, $\Delta\sigma_I = \Delta\sigma_R$ and presumably ∇^X and $\bar{\nabla}^X$ are simply related, even though we continue to see donor-acceptor properties in the resonance-inductive modes. In general, however, as pictured, the inductive and resonance capabilities of substituents appear unrelated, and thereby ∇^X and $\bar{\nabla}^X$ (and σ_I and σ_R) are assumed independent variables.

As a final point in this regard, it is of interest to note that the resonance model coefficients, -12.5 and -15.1 x 10⁻³ for m- and p-position substitution (see footnote 19) are considerably smaller than those for the inductive model. If these estimates are of the correct order, it might be argued that in making a change from sp² carbon to a group, X, the sensitivity of the π -orbital on X to the change is several times ($\sim 8x$) that experienced at the neighboring ring atom, or about equal, with $\epsilon = 1/10$, to that felt in the σ -orbitals of X. This number is obtained by adjustment of the resonance coefficient to equal the inductive coefficient, as in Taft's p-substituent cases, thereby equally scaling the deltas: the result seems intuitively

quite reasonable and consistent with respect to the value of unity previously taken for C, the π -, σ -coupling factor.

D. Statistical Test of the I-Effect Theory

Having rationalized the proportional carry-over of σ^* to σ_I for model systems, implications of this result to real reactivities were statistically examined. Table V contains the least-squares results for the σ^0 -reactivities with K_I held at 0.87 and 1.00, and with σ_I held to Taft's values. In both cases, K_R was initially specified as 2.0, although upon further testing with values as high as 4.0, the fit upon convergence was found to be essentially the same. In both cases shown, the optimum K_R was found to be 2.10 ± 0.05 and the SD of fit was 0.030. Somewhat higher converged values of K_R were found with higher starting values for this parameter, and were generally accompanied by σ_R values of greater magnitude.

The comparisons of most interest are the changed proportion of the total effect found in I and R in going from K_I of unity to 0.87. For the m-position cases, there is an average of 12% decrease in I-increase in R; for the p-position cases the shift is $\sim 17\%$. These numbers are derived by averaging the shifts in I with those in R between the two K_I -set results, recognizing that decreased I and increased R (or visa versa, depending on the signs of the parameter couples, $\rho\sigma$) shifts one of these effects into the other. The comparable shifts from theory where the π -inductive effect is removed from I and placed in R are, for m-cases $\sim 7\%$ (7 parts in 107) and for the p-cases $\sim 16\%$ (16 parts in 103).

The agreement between the statistical and theoretical results are satisfactory; interpretation of the meanings of these results is however not comparably satisfying. As previously noted for the runs where σ_I 's were allowed to go free, ρ_R^P/ρ_I^P is again essentially constant for a given K_I , but varies upon change of K_I , i.e., $\rho_R^P/\rho_I^P \cong 1$ for $K_I = 1.00$ and $2/3$ for $K_I = 0.87$. As well, the sets of σ_R generated appear essentially proportional. When the transformation equations in Appendix A-3 are examined, the mechanics of the shift are understood. Examination of Table VI indicates substantially identical results are obtained for the σ -type reactivities.

In the absence of the transformation relationships shown in the Appendix, it would have been difficult to escape the conclusion that σ_I and σ_R were dependent. They would, in fact, have had to be linearly related, so that shifting of I into R could be accomplished without change in precision of fit. This would have provided anomalies as regards the theoretically rationalized differences between I and R and, more directly, a plot of σ_I vs. σ_R for the substituents of present concern in particular, and all substituents in general. These anomalies are happily avoided.

At the same time, we are presented with the challenge of interpreting the variation in ρ_R^P/ρ_I^P with change in division of I and R. Upon hypothesizing a separation where all effects either propagated by or transmitted by the π -framework are included in R, the relative sensitivity to resonance (as now defined, compared to classical inductive) effects is found to decrease, compared to the more usual separation. If the statistics are meaningful, and they appear to be so as evidenced by the essentially identical fittings obtained in the different (K_I value) cases, this may be an entirely reasonable

Table V

Comparative Statistics for the σ^o Reactivity Serieswith $K_I = 1.00$ and 0.87^a

Reaction	ρ_I^m		ρ_R^m	
	For $K_I = 1.00$	0.87	1.00	0.87
1	2.05 ^b	1.97	1.01	0.53
2	0.48	0.46	0.22	.11
3	.22	.20	.13	.07
4	1.07	1.02	.55	.28
5	0.70	0.67	.37	.19
6	1.03	.97	.58	.30
7	-2.68	-2.53	-1.40	- .71
8	.38	.38	.15	.08
9	.95	.94	.37	.19
10	.64	.61	.29	.15
11	.52	.50	.26	.14
12	.82	.79	.41	.21
13	1.01	.96	.54	.28
14	1.26	1.20	.60	.30
15	-0.29	-0.26	- .20	- .10
16	- .66	- .61	- .41	- .21
17	- .20	- .19	- .10	- .05

Substituent Constants

	OCH ₃	CH ₃	F	Cl	NO ₂
σ_I (held)	0.26	-.05	0.52	0.46	0.63
σ_R (initial)	-.42	-.10	-.33	-.19	.18
for $K_I = 1.00$	-.40	-.08	-.37	-.19	.20
= 0.87	-.65	-.15	-.54	-.23	.54

$$^a \quad \rho_I^p = K_I \rho_I^m; \quad \rho_R^p = K_R \rho_R^m$$

K_R (initial) = 2.0 for both runs; K_R (SD) converged = 2.04 (0.0299)
and 2.15 (0.0298) for $K_I = 1.00$ and 0.87 , respectively.

^b Standard reaction, this ρ_I^m held.

Table VI

Comparative Statistics for the Benzoic-Type Reactivity Series

with $K_I = 1.00$ and 0.87^a

Reaction	ρ_I^m		ρ_R^m	
	For $K_I = 1.00$	0.87	1.00	0.87
18	1.00	0.91	0.60	0.17
19	1.58	1.49	.82	.24
20	1.72	1.59	1.05	.31
21	1.22	1.14	.71	.21
22	1.36	1.27	.74	.22
23	1.48	1.39	.80	.23
24	1.26	1.19	.69	.20
25	1.39	1.31	.76	.22
26	1.56	1.47	.80	.23
27	1.52	1.43	.82	.24
28	1.47	1.37	.81	.24
29	0.92	0.86	.50	.14
30	2.34	2.16	1.37	.40
31	2.48	2.30	1.44	.42
32	2.57	2.40	1.42	.42
33	0.44	0.40	0.27	.08
34	1.26	1.17	.73	.21
35	0.75	0.69	.46	.13
36	.65	.60	.40	.12
37	3.08	2.84	1.89	.55
38	1.79	1.62	1.25	.36
39	1.69	1.59	0.88	.26
40	.40	0.37	.27	.08
41	.44	.41	.27	.08

Substituent Constants

	OCH ₃	CH ₃	F	Cl	NO ₂
σ_I (held)	0.26	-.05	.52	.46	.63
σ_R (initial)	-.42	-.10	-.33	-.19	.18
for $K_I = 1.00$	-.39	-.06	-.32	-.16	.14
0.87	-1.18	-.23	-.82	-.32	.76

^a Footnotes of Table V apply with K_R (SD) converged = 2.28 (0.0389) and 2.35 (0.0388) for $K_I = 1.00$ and 0.87 , respectively.

result. Since all effects of a substituent must be fundamentally related, and since the linear free energy equation can only recognize the simplest of relations between effects which are empirically separated, e.g., linearity in σ_I and σ_R , variations in sensitivity factors to the separated effects may be expected upon change in the divisions of such effects.

The implications of this analysis to the ultimate question of whether I and R are truly separable is obvious. Extension of these methods to reactivity systems where enhanced and levelled effects are known to occur is desirable, both to test concepts and to better define the practical limits of the statistical methods employed. Such extensions are presently under consideration.

Appendix

A-1 Conditions for Obtaining Unique Parameter Sets

$$\text{For, } \log k/k_0 = \rho_I \sigma_I + \rho_R \sigma_R$$

$$\text{with } \begin{aligned} \rho &= f \text{ (reaction, position of substitution)} \\ \sigma &= f \text{ (substituent)} \end{aligned}$$

where the ρ 's and σ 's are assumed to be totally independent of each other and exactly fitted to the data or best fitted by least-squares procedures, one may construct alternative sets of parameters, ρ' , by linear combinations,

$$\rho_I' = a \rho_I + b \rho_R$$

$$\rho_R' = c \rho_I + d \rho_R$$

which are also functions only of reaction and substitution position. The corresponding σ -parameters are then,

$$\sigma_I' = (d \sigma_I - c \sigma_R) / (ad - bc)$$

$$\sigma_R' = (a \sigma_R - b \sigma_I) / (ad - bc)$$

Unique determination of parameter sets thereby requires conditions which fix a, b, c and d. In contrast, the Hammett equation, $\log k/k_0 = \rho \sigma$, requires only one constraint, i.e., if $\rho' = \bar{a} \rho$, then $\sigma' = \sigma / \bar{a}$ and only $\bar{a}$ must be fixed. The latter is accomplished by definition of a standard reaction: (ρ for benzoic acid ionizations in H_2O at 25° taken as unity).

Under the Taft constraints, the "mixing parameters" a-d are fixed as follows:

$$\rho_I^m = \rho_I^p = \rho_I$$

$$\rho_R^m = \alpha \rho_R^p$$

$$\rho_R^p = \rho_I$$

$$(\rho_I)_{SR} \equiv 1.000$$

$$a + b\alpha = (\rho_I^m)_{SR}$$

$$c + d\alpha = (\rho_R^m)_{SR}$$

$$a + b = (\rho_I^p)_{SR}$$

$$c + d = (\rho_R^p)_{SR}$$

$$\text{and } \frac{\alpha \rho_I^{p'} - \rho_I^{m'}}{\alpha \rho_R^{p'} - \rho_R^{m'}} = \text{constant} = \frac{a}{c}$$

Here SR denotes the standard reaction; the last relationship on the right implies constancy over all reactions and corresponds to $\rho_R^m = \alpha \rho_R^p$. In the present studies:

$$\begin{aligned} \rho_I^p &= K_I \rho_I^m \\ \rho_R^p &= K_R \rho_R^m \\ (\rho_I^m)_{SR} &\equiv 1.000 \\ (\sigma_R)_{SS} &= \sigma_R \text{ (Taft)}_{SS} \end{aligned} \quad ; \quad \begin{aligned} d(\rho_I^{m'})_{SR} - b(\rho_R^{m'})_{SR} &= ad - bc \\ \frac{K_I \rho_I^{m'} - \rho_I^{p'}}{K_I \rho_R^{m'} - \rho_R^{p'}} &= \text{constant} = \frac{b}{d} \\ \frac{K_R \rho_I^{m'} - \rho_I^{p'}}{K_R \rho_R^{m'} - \rho_R^{p'}} &= \text{constant} = \frac{a}{c} \\ b(\sigma_I')_{SS} + d(\sigma_R')_{SS} &= \sigma_R \text{ (Taft)}_{SS} \end{aligned}$$

SS signifies a substituent chosen as standard with σ -value (here σ_R) held invariant.

A-2 Where different parameter sets are generated with different K_R at constant K_I .

Presume, $\sigma_I + \sigma_R = \text{constant} \{f(\text{substituent})\} = \sigma_I' + \sigma_R'$
where $\rho_R^p / \rho_I^p = \rho_R^{p'} / \rho_I^{p'} = 1$; and $\rho_I^p = \rho_I^{p'}$

$$\begin{aligned} \rho_I^{p'} &= (a + b) \rho_I^p & a + b &= 1 \\ \rho_R^{p'} &= (c + d) \rho_I^p & c + d &= 1 \\ \rho_I^{m'} &= \left(\frac{a}{K_I} + \frac{b}{K_R} \right) \rho_I^p & a + \frac{b}{K_R} &= 1 \\ &= \rho_I^{p'} / K_I \\ \rho_R^{m'} &= \left(\frac{c}{K_I} + \frac{d}{K_R} \right) \rho_I^p & \frac{c}{K_I} + \frac{d}{K_R} &= \frac{1}{K_R'} \\ &= \rho_R^{p'} / K_R' \end{aligned}$$

or, $a = 1$, $b = 0$, $c = (y-x)/(1-x)$, $d = (1-y)/(1-x)$, where $y = K_I/K_R'$ and $x = K_I/K_R$.

$$\begin{aligned} \sigma_I + \sigma_R &= \sigma_I' + \sigma_R' = [(d - b)\sigma_I + (a - c)\sigma_R] / (ad - bc) \\ \sigma_I' + \sigma_R' &= \left[\frac{(1-y)}{(1-x)} \sigma_I + \left(1 - \frac{y-x}{1-x}\right) \sigma_R \right] \bigg/ \frac{1-y}{1-x} = \sigma_I + \sigma_R \end{aligned}$$

The transformation conditions check; σ_I and σ_R are analytically transformable knowing K_R' .

A-3 Where different parameter sets are generated, holding σ_I constant, for different K_I .

$$\text{Here, } \rho_R^{P'} / \rho_I^{P'} = \ell' \text{ for } K_I' \text{ set and } \rho_I^{P'} = m \cdot \rho_I^P$$

In a similar fashion to A-2

$$\begin{aligned} a + b &= K_I' m & c + d &= \ell' \cdot K_I' m \\ \frac{a}{K_I} + \frac{b}{K_R} &= m & \frac{c}{K_I} + \frac{d}{K_R} &= \frac{\ell' \cdot K_I' m}{K_R} \end{aligned}$$

With $K_I = 1.00$

$$a = m(K_R - K_I') / (K_R - 1), \quad b = m(K_I' - 1)K_R / (K_R - 1), \quad c = 0, \quad d = m\ell'K_I'$$

$$\sigma_I' = \frac{1}{a} \sigma_I, \quad \sigma_R' = \frac{1}{d} \left(\sigma_R - \frac{b}{a} \sigma_I \right)$$

For the case discussed $\ell' \approx 2/3$, $m = 1/1.04$ with $K_I' = 0.87$: $K_R = K_R' = 2.1$. Therefore, $a \approx 1.0$ or, $\sigma_I' = \sigma_I$, as required, and,

$$\sigma_R' = 1.8(\sigma_R + 0.26\sigma_I)$$

When σ_R' versus $(\sigma_R + 0.26\sigma_I)$ is plotted, fitting by a straight line is somewhat better than σ_R' vs. σ_R .

B. σ^0 - and σ -Reactivity Sets

Reactions 1-12 are as listed in ref. 2. Reactions 13-17 are respectively: ionization of $\text{ArCH}_2\text{NH}_2^+$ in H_2O ; hydrogen bond equilibrium in CCl_4 of sub. phenols with pyridine; $\bullet\text{CCl}_3$ addition and abstraction reactions with $\text{X}\phi\text{CH}_2\text{CH}=\text{CH}_2$ and addition to $\text{X}\phi(\text{CH}_2)_2\text{CH}=\text{CH}_2$. These comprise the σ^0 -set.

Reactions 18-41 are σ^- , or benzoic-reactivities and are in order: ionization (ion) of benzoic acid in H_2O and EtOH and ion of 2-Me benzoic acid in EtOH at 50° ; ion of benzoic acid in 26.5, 43.5, 73.5% dioxane, in Et glycol, in MeOH, EtOH, *i*-PrOH and *t*-BuOH at 25° ; $\text{ArCO}_2\text{H} +$ diphenyldiazomethane; saponification of ArCO_2Et in aqueous acetone and EtOH; trans esterification of $\text{ArCO}_2\text{C}_{10}\text{H}_{19}$ with OMe^- ; ion of cinnamic acids in H_2O , saponification of its ethyl esters in EtOH; ion phenyl propiolic acids in aqueous dioxane and EtOH; hydrolysis of acetic anhydrides; saponification of phthalides; ArCO_2H dissociation in Me cellosolve; cinnamic acid + diphenyldiazomethane in EtOH at 25° and 35° .

References and Footnotes

1. Work conducted under the auspices of the U. S. Atomic Energy Commission.
2. S. Ehrenson, Tetrahedron Letters, 7, 351 (1964).
3. See, R. W. Taft, Jr., and I. C. Lewis, J. Am. Chem. Soc., 81, 5343 (1959) as a prime reference relating to the work under discussion here.
4. S. Ehrenson, "Theoretical Interpretations of the Hammett and Derivative Structure-Reactivity Relationships," "Progress in Physical Organic Chemistry," S. Cohen, et al., eds., Interscience Publishers, New York, N. Y., 1964
5. H. O. Hartley, Technometrics, 3, 269 (1959).
6. Cf., L. I. Hodson and J. S. Rollett, Acta Cryst., 16, 329 (1963) where the block-diagonal procedure is discussed and additional references mainly concerned with crystal structure determinations, are presented.
7. With m reactions and n substituents, with one ρ_I^m set and held for a standard reaction and with one σ_R (or σ_I) set and held for a standard substituent, there are $(2m-1)$ ρ 's and $(2n-1)$ σ 's plus 2 K's to determine. Further constraints of course increase the data per parameter ratio.
8. Input K_I and K_R respectively 0.75-1.3 and 2.0-3.0.
9. For changing K_R at constant K_I , from Appendix A-2, para $\rho_I^p \sigma_I \rightarrow \rho_I^p \sigma_I'$, $\rho_R^p \sigma_R \approx \rho_I^p \sigma_R \rightarrow \rho_I \sigma_R'$; meta, $\rho_I^m \sigma_I = \rho_I^p \sigma_I / K_I \rightarrow \rho_I^p \sigma_I' / K_I = \rho_I^m \sigma_I'$, $\rho_R^m \sigma_R = \rho_R^p \sigma_R / K_R \approx \rho_I^p \sigma_R / K_R \rightarrow \rho_I^p \sigma_R' (K_R / K_R') / K_R = \rho_I^p \sigma_R' / K_R' \approx \rho_R^p \sigma_R' / K_R' = \rho_R^m \sigma_R'$.
10. In the case of electrostatic transmission assuming r^{-1} dependence (in the monopole-monopole modification of the Kirkwood-Westheimer model), with poles located at the ring sites, the p/m -effect ratio corresponds to $K_I = 0.87$; for the K. W. model with the moment of the dipole on the ring, the result is again 0.87; for the center of the dipole one-half a benzene bond length from the ring, 0.94. The same average dielectric is assumed for paths from both positions. Similar results are obtained in the bond transmission model with damping factors per bond of $\sim 1/2$.
11. Cf., C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 65.
12. K. B. Everard and L. E. Sutton, J. Chem. Soc. 2821 (1951).
13. R. W. Taft, Jr., and H. D. Evans, J. Chem. Phys., 27, 1427 (1957).
14. (a) D. Peters, J. Chem. Soc., 2654 (1957).
(b) O. Exner, Tetrahedron Letters, 6, 815 (1963).

15. The monopole-monopole model is used for all electrostatic interactions; it certainly is preferable as the distance between the interacting sites decreases.¹⁶ An extremely important point concerning the size of ϵ is also raised. If ϵ is large (weak damping), the effects arising at X and Y are propagated for substantial distances. This being the case, the electrostatic model would be expected to break down and, more importantly from an observational point of view, the effects of X and Y would necessarily be inseparable, especially as regards linear free energy substituent-reaction center effects, because of X,Y cross-terms. If, on the other hand, ϵ is small, equation 6 may be truncated after the first-power term in ϵ , and in neither m- or p-disubstituted benzene cases would cross-terms be of importance. (The implications to small molecules where X and Y are proximate are clear.) It is further of interest that this model predicts a p-/m- classical I-effect ratio essentially the same as that from the simple electrostatic models previously discussed, and, as a result, operationally indistinguishable from pure through-the-bonds models (with weak damping), on the basis of this ratio alone.⁴ The present model is, however, capable of rationalizing the need for strong damping to explain such phenomena as quadrupole-coupling effects of substituents,¹⁷ which neither the simple electrostatic models nor single- ϵ through-the-bonds models reasonably can explain.

For meta-disubstituted benzene as pictured, with Y as site 1, RX as site 4, all bonds of benzene C-C length, r_0 , and ϵ independent of the nature of the bond (vide infra),

$$\frac{D E_{CI}}{e_{RX} e_Y} = \frac{1}{r_{14}} + \epsilon \left(\frac{1}{r_{13}} + \frac{1}{r_{15}} + \frac{1}{r_{24}} \right) = \frac{1}{r_0} (0.378 \pm 1.488 \epsilon),$$

and for the para-disubstituted molecules with the same substituents,

$$\frac{D E_{CI}}{e_{RX} e_Y} = \frac{1}{r_{15}} + \epsilon \left(\frac{2}{r_{14}} + \frac{1}{r_{25}} \right) = \frac{1}{r_0} (0.333 + 1.256 \epsilon).$$

The factor $1 + (3.85 \pm 0.09)\epsilon$ may be factored out of each parenthesized quantity, leaving a p-/m- ratio of ~ 0.87 , essentially independent of ϵ . While indistinguishable, because of this ratio, from the pure framework transmission model with $\epsilon \sim 1/2$ (see discussion on this point for the simple electrostatic model in ref. 4), the cross-term problem is here avoided for small ϵ ($\sim 1/10$). Further, it is entirely reasonable that for reactivities and F n.m.r. shifts,¹⁸ both inductive effects in combination contribute, requiring large ϵ if the framework model is to be substituted to account for the whole effect. On the other hand, quadrupole coupling constants may importantly depend only upon the polarization of the bond to the atom whose quadrupole moment is observed, i.e., to interactions having a given symmetry (σ^- , as here postulated). In this case, the framework model is alone correct, and the small ϵ -value pertains.

16. M.J.S. Dewar and P. J. Grisdale, J. Am. Chem. Soc., **84**, 3539 (1962).
 17. H. O. Hooper and P. J. Bray, J. Chem. Phys., **33**, 334 (1960).
 18. R. W. Taft, Jr., J. Am. Chem. Soc., **79**, 1045 (1957); however, also see H. Spieseke and W. G. Schneider, J. Chem. Phys., **35**, 722, 731 (1961) where strong damping is required to rationalize Cl³⁵ n.m.r. effects.

19. A_I is proportional to the atom-atom polarizabilities for sites RX and RY (or Y) in the zeroth-order (non-self-consistent) approximation.
20. The A_I coefficients obtained as described in ref. 4 were checked by complete Wheland-Mulliken secular equation solution with self-consistent charge redistribution for benzyl radical-type structures perturbed at the terminal site and at its neighbor. The comparable A_I results of -6.6 and -15.3×10^{-3} were obtained. Of further interest, it was found that the perturbation theory presumption of additivity of terminal atom and neighbor atom effects is essentially correct: the complete solution for both positions perturbed yields -16.1 and -28.3×10^{-3} for the m- and p-case coefficients respectively, and for the terminal perturbation alone, -9.5 and -13.0×10^{-3} . The perturbation theory results for the latter are -12.5 and -15.1×10^{-3} .
21. (a) R. P. Iczkowski and J. L. Margrave, J. Am. Chem. Soc., **83**, 3547 (1961).
(b) R. S. Mulliken, J. Chem. Phys., **2**, 782 (1934).
22. Cf., H. C. Longuet-Higgins and C. A. Coulson, J. Chem. Soc., 971 (1949): values on this order are required to correlate bond dipole moments and the previously mentioned quadrupole coupling effects.
23. S. Ehrenson, J. Phys. Chem., **66**, 706, 712 (1962).
24. N. Muller, L. W. Pickett and R. S. Mulliken, J. Am. Chem. Soc., **76**, 4770 (1954).
25. J.A.A. Ketelaar and G. W. van Oosterhout, Rec. trav. chim., **65**, 448 (1946).
26. The specific numerical illustration for the σ^0 -reactivities may be generalized. The relative contributions of the two terms is not expected to change much for other reactivities. The A_I values for m- and p-substituted benzyl-type structures, which reflect the π -inductive effects for xylylene-type molecules (models for conjugating X and Y groups) are not much different from those for the benzene-type structures considered above for π -induction in the σ^0 -reactivities.
27. Cf., E. Clementi, J. Chem. Phys., **36**, 33 (1962): also see further discussion of this question with regard to alkyl group effects in S. Ehrenson, J. Am. Chem. Soc., **86**, 847 (1964).