[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

Theoretical Considerations Concerning the Hammett Equation. VI. A Molecular Orbital Treatment of the Multiplicity of Substituent Constants[1]

BY H. H. JAFFÉ[1a]

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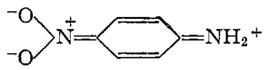
Distinct substituent constants (σ) are required for several electron attracting substituents. Two molecular orbitals (MO) treatments of substituent constants are used to investigate the relation between "normal" substituent constants and σ^*-values. Coulomb integrals evaluated by use of the hypothesis that σ-values are proportional to electron density changes induced by substituents at the respective *ring* atoms in monosubstituted benzenes are used to evaluate the electron density changes (δq) induced in *side chain* atoms. The δq-values so calculated for the *meta*-substituted compounds are accurately proportional to σ-values, but no relation between δq and σ^* is observed for the *para* compounds. This fact is attributed to difficulties in the MO treatment. The same Coulomb integrals are used to calculate the effect of substituents on the localization energies for localization of an electron pair at the side chain atom in benzyl anions. The localization energy changes are nearly proportional to the σ-values for the *meta* compounds, and to the σ^*-values for the *para* compounds.

Ever since the Hammett equation was first proposed it has been realized that certain electron attracting substituents in the *para* position require the use of two distinct σ-values for different types of reactions.[2] Thus Hammett reported two substituent constants for the *p*-nitro group, one applicable to reactions of anilines and phenols ($\sigma^* = 1.27$),[3] the other applicable to other reactions ($\sigma_p = 0.778$). Separate σ- and σ^*-values have since been proposed for several other groups.[4] It has long been believed that this duality of substituent constants is related to the relative importance of resonance structures of the general type of structure I in the derivatives of aniline and phenol.[5,4] In the present paper an attempt will be made to provide a molecular orbital (MO) interpretation of this duality of substituent constants.

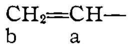


I

Two wave-mechanical methods have been proposed for the theoretical treatment of substituent constants. The first is based on the hypothesis that σ-values are proportional to the electron density changes induced by substituents at the ring carbon atom at which the reacting side chain is attached.[6] The second method depends on the calculation of the effects of substituents on localization energies[7] in reactions involving localization of an electron pair or a vacant π-orbital at a side chain atom (*cf.* structures IV and V, below). Such localization energies are believed to be measures of the corresponding activation energies,[8] and thus this method relates substituent constants with activation energies. The first method suffers from the difficulty that it requires the theoretical or semi-empirical evaluation of certain parameters occurring in the MO calculations. In the second method it has been found possible to neglect much of the resonance effects, and hence to evaluate the parameters more readily from physical measurements.

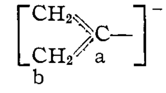
In this paper we attempt to relate σ^*-values to the molecular orbital description of the corresponding substituents. For this purpose we shall evaluate the parameters required for the MO description of a substituent X by use of the hypothesis that substituent constants are proportional to the electron density changes produced by the substituent at the *ring* carbon atom bearing the side chain.[1,6] These parameters will then be used in the calculation of electron density changes produced by the same substituents in *side chain* atoms, and of changes of localization energy when a side chain atom is removed from the conjugated system.

Parameters.—The evaluation of the parameters was performed by perturbation theory[9] in the manner used in an earlier paper.[1] The substituents treated here could be considered as derived by a perturbation from the vinyl group II or the group III; the letters a and b indicate the manner in which the atoms will be designated. The MO treatment of the compounds C_6H_5X, with X either II or III, requires four parameters, the coulomb integrals α_a and α_b, and the resonance integrals β_{ab} and β_{aC}. However, the compound $C_6H_5CH{=}CH_2$ is an alternant hydrocarbon; hence all atom bond polarizabilities vanish for this compound, and the electron densities are independent of the resonance integrals.[10] The compound C_6H_5X, with X = III, is an alternant hydrocarbon ion[11]; for such compounds it has been shown that the polarizability $\pi_{r,st}$ for atom r by bond st vanishes whenever the coefficient c_{r0} with which atom r enters into the zero energy MO vanishes. The



$\underset{b}{CH_2}{=}\underset{a}{CH}{-}$

II



III

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[1] For paper V, see H. H. Jaffé, THIS JOURNAL, **76**, 3527 (1954).

[1a] Department of Chemistry, University of Cincinnati.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

[3] As proposed in a recent review paper (ref. 4) the symbol σ^* will be used to designate substituent constants for use with reactions of anilines and phenols. This should not be confused with the constant designated as σ^* by R. A. Taft, Jr., THIS JOURNAL, **75**, 4231 (1953), which has an altogether different significance.

[4] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953), and references cited there.

[5] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1945, p. 250.

[6] H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 778, 1554 (1952).

[7] F. L. J. Sixma, *Rec. trav. chim.*, **72**, 673 (1953).

[8] R. D. Brown, *Quart. Revs.*, **6**, 63 (1952).

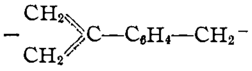
[9] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947).

[10] C. A. Coulson and H. C. Longuet-Higgins, *ibid.*, **A192**, 16 (1947).

[11] H. H. Jaffé, *J. Chem. Phys.*, in press.

TABLE I

ELECTRON DENSITY AND LOCALIZATION ENERGY CHANGES INDUCED BY SUBSTITUENTS (R)

R	σ_p^a	σ_m^a	σ^{*a}	α_a^b	α_b^b	Electron density method δq_p^c	Electron density method δq_m^c	Electron density method $\xi^{*d}_{calc.}$	Localization method δL_p	Localization method δL_m	Localization method $\xi^{*d}_{calc.}$	$\xi^{*d}_{exp.}$
a. Reference compound: $CH_2{=}CH{-}C_6H_4{-}CH_2^-$												
CHO	0.216	0.382	1.126	1.609	−0.356	0.1175	0.0353	3.33	0.083	0.046	1.80	2.95
$COCH_3$	.516	.306	0.874	1.332	.043	.1570	.0311	5.05	.118	.038	3.11	2.86
CN	.628	.678	1.000	2.886	− .397	.1882	.0646	2.91	.143	.086	1.66	1.47
COOH	.265	.355	0.728	1.503	− .179	.1360	.0338	4.02	.099	.044	2.25	2.05
$COOC_2H_5$	.522	.398	0.578	1.717	− .211	.1443	.0386	3.74	.106	.050	2.12	1.45
b. Reference compound:  $-\begin{matrix}CH_2\\ \\ CH_2\end{matrix}\!>\!C{-}C_6H_4{-}CH_2^-$												
NO_2	0.778	0.710	1.270	3.131	−1.246	0.1127	0.0713	1.58	0.164	0.106	1.55	1.79
COOH	.265	.355	0.728	1.544	−0.818	.0610	.0344	1.77	.092	.057	1.61	2.05
$COOC_2H_5$	.522	.398	0.578	1.773	− .566	.0897	.0409	2.19	.113	.064	1.77	1.45

[a] From reference 4. [b] In units of β. The coulomb integral of ring carbon atoms $\alpha_C{=}O$ defines the origin of the energy scale. [c] In units of the electronic change. [d] $\xi^* = \sigma^*/\sigma_{meta}$.

data tabulated in the appendix[14] show that this condition is fulfilled for the *m*- and *p*-positions. Accordingly, in the compounds treated here, the electron densities in the *m*- and *p*-positions depend only on the coulomb integrals α_a and α_b, and the two substituent constants (σ_{meta} and σ_{para}) are sufficient to evaluate these two parameters.

The groups $-COOH$ and $-COOC_2H_5$ were treated as perturbed forms of both structures II and III, and in the latter case both oxygen atoms were assumed equal. The results of the two treatments do not differ greatly. The parameters derived in this manner are tabulated in Table I.

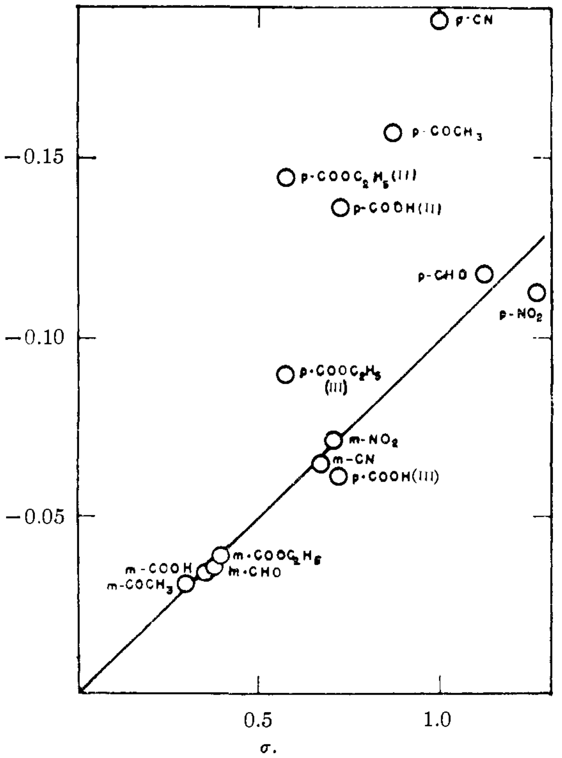
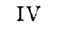


Fig. 1.—The relation between electron density changes and substituent constants. No separate points for either the *m*-COOH or the *m*-$COOC_2H_5$ group treated by means of models II or III are given, since the difference between such pairs of points is negligible.

Electron Density Method (Static Method).—As a first approximation we have calculated the effect of introducing a substituent into the *meta* and *para* position of the benzyl anion ($C_6H_5CH_2^-$) on the electron density at the methylene carbon atom. The benzyl anion was chosen as the test compound since this ion is the reference structure (unperturbed structure) for calculations for aniline and phenol by perturbation theory.[9] The results of the calculations are shown in Fig. 1 and in Table I, where it is seen that the electron density changes for all the *meta* compounds are accurately proportional to the corresponding substituent constants. The electron density changes for the *para* compounds, however, appear to bear no relation to the σ^*-values; in most cases the electron density changes calculated appear appreciably too large. This discrepancy is undoubtedly due to the neglect of the perturbation of the resonance integrals β_{ab} and β_{aC}. It has been shown that, in the reference compounds used here which are alternant hydrocarbons ions,[11] the atom bond polarizabilities vanish only under special circumstances. Comparison of the theorems reported elsewhere[11] with the c_{rj} reported in the appendix[14] shows that these polarizabilities vanish for the *meta* compounds, but not for the *para* isomers. Unfortunately, no data are available to permit a ready evaluation of the relevant resonance integrals.

Localization Theory.—In the calculations using localization theory we have again used the substituted benzyl anions as a test case; in the framework of this method this choice is well justified since Sixma found that results for calculations with the benzyl anion, the benzyl cation and aniline gave essentially identical results.[7] The quantity of interest here is the change δL in localization energy L produced by introduction of a substituent. The localization energy is the difference between the π-electron energies of structures IV and V, where the dotted lines indicate the extent of the conjugated system. The resonance integral of the extracyclic bonds affects the localization



IV

V

energy changes only through the following differences in bond order: (1) the difference of the order of the ring–methylene bond between unsubstituted and substituted compounds; (2) the difference in bond order of the bonds ab and aC within the substituent between localized and non-localized structures (IV and V). There is no reason to believe that these differences should not be small; hence we have neglected perturbations of bond orders in the localization calculations. Accordingly, we have introduced the parameters obtained above into these calculations. The results are shown in Table I and Fig. 2. It is seen that the points for the *meta* compounds do not fall on a single line; they define two closely spaced parallel lines; the points arising from substituents represented by structures II and III each define a separate line. Most of the points for the *para* compounds fall within the band defined by these two lines. Only the point for the formyl group deviates widely from this band.

Discussion

The calculations by the electron density method for the *meta*-substituted compounds confirm the earlier concept that substituent constants are related to the effects of substituents on the electron density at the reacting center.[2,4,6] Unfortunately, the calculations of electron density changes for the *para*-substituted compounds depend so strongly on the resonance integrals that the calculations are of little value.

It is encouraging to find that the localization calculations for the *m*-substituted compounds give localization energy changes nearly proportional to the corresponding substituent constants, although the calculations are based on parameters derived from the electron density method. This fact is undoubtedly closely related to the fact that both methods *usually* give the same results in calculations of chemical reactivity (*cf.* Brown's "chemical non-crossing rule").[1,8] The results obtained for the *para* compounds appear in as good agreement with σ^*-values as might have been hoped for if it is recalled that the comparisons depend on three experimental substituent constants, each of which is affected by an uncertainty of about ±0.05 units.[12] The only widely diverging value is that for the formyl group. No explanation of this divergence can be proposed, unless the substituent constants should be appreciably in error.[13]

The successful correlation of σ^*-values with localization energy changes shown in Fig. 2 indicates that the proposed interpretation of the multiplicity of substituent constants is essentially correct.[4,5] Accordingly, calculations similar to those reported here may be expected to give reasonable results with electron repelling substituents (*e.g.*, the *p*-hydroxy and *p*-dimethylamino groups), for which a similar multiplicity of substituent constants has been observed.[4] No calculations for such cases are reported here since no single substituent constants have been proposed for these substituents when in the *para* position with respect to electron attracting side chains, and since therefore no simple experimental data are available for correlation with the calculations.

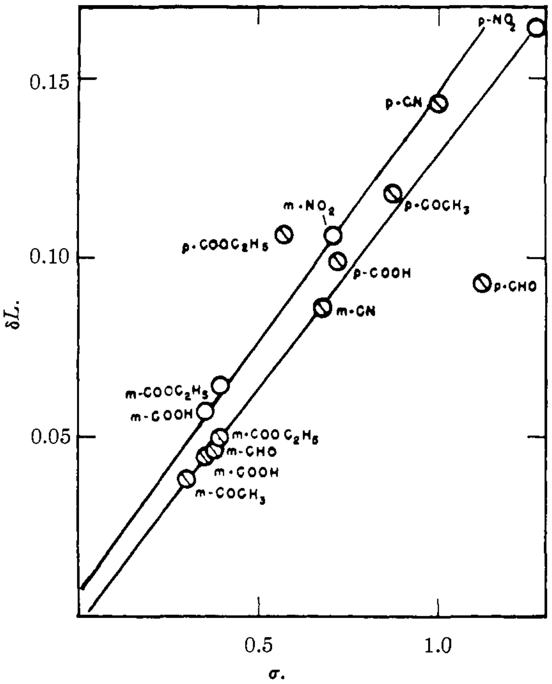


Fig. 2.—The relation between localization energy changes and substituent constants. The crossed points refer to model II, the open ones to model III.

Calculations.—All calculations were performed by first-order perturbation theory[9,10] applied to the LCAO MO method, neglecting overlap integrals. This very crude approximation was chosen since the computations become prohibitively extensive in any better approximation. The considerable success achieved in calculations of reactivities with this approximation[1,6-8] is the only justification for its use.

The wave functions, orbital energies (ϵ_j), charge densities (q_r) and atom–atom polarizabilities ($\pi_{r,s}$) for all unperturbed structures used are tabulated in an appendix.[14]

For the evaluation of coulomb integrals (α_r) two simultaneous linear equations of the form of equation 1 were set up[15] and solved for α_a and α_b.

$$\sigma_r/\kappa = \delta q_r = \pi_{b,r}\alpha_b + \alpha_a\Sigma_s\mathcal{E}^n{}_s\pi_{s,r} + \delta q_r{}^0 \qquad (1)$$

with r = *meta* or *para*. The proportionality constant $\kappa = -15.5$ was taken from earlier papers in this series.[6] The term $\mathcal{E}^n{}_s$, with $\mathcal{E} = {}^1/_3$, arises out of the treatment of the inductive effect,[6] and is discussed below.[16] $\delta q_r{}^0$ is the difference in electron density at atom r between the substituted and unsubstituted unperturbed structures, *i.e.*, in this case between C_6H_5X and C_6H_6. The summation extends over all atoms of the conjugated system except for atom b. All

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[12] See Table VIII of reference 4.

[13] A careful reexamination of the available data suggests that the σ^*-value for the CHO group is somewhat too large. A value somewhat below 1.0 would probably fit the majority of reaction series somewhat better. However, a correction of the σ^*-value alone in this manner would not eliminate the observed discrepancy. Unfortunately, there are almost no experimental data available for checking the other two substituent constants for this group.

[14] The Appendix has been deposited as Document number 4308 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints or $1.75 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress. The mutual atom polarizabilities for $C_6H_5CH_2$ are given in reference 1.

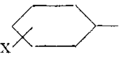
[15] Terms in $\pi_{r,st}$ were not included since the relevant $\pi_{r,st}$ vanish (*cf.* above).

[16] *Cf.* also H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953), and reference 6.

electron densities are expressed in units of the electronic charge.

Equation 1 was then used in the reverse direction to calculate the values of $\delta q_{CH_2^-}$ induced by introduction of substituents into the benzyl anion. Localization energy changes were calculated by equation 2.[17]

$$\delta L = \delta L^0 + \delta q_b \alpha_b + \alpha_a \Sigma_s \mathcal{E}_s \delta q_s \qquad (2)$$

Here, δL° is the difference in localization energy between the substituted and unsubstituted reference structures, in this case  —CH_2^- and $C_6H_5CH_2^-$, and the δq_r are the difference in electron density at atom r between the unperturbed non-localized and localized structures, IV and V, respectively. All localization energies are expressed in units of β, the CC resonance integral appropriate for a ring bond.

Inductive Effect.—Throughout this paper the inductive effect has been treated in the manner proposed in the earlier papers of this series.[6] It was there shown that the inductive effect is of major importance in the electron density method. This is apparent from equation 1, where the terms in powers of $\mathcal{E}$ decrease with n_s, but the polarizabilities are largest for s = r, and generally the less important the farther s and r are separated. In the localization method the results do not depend greatly on the assumptions made about the inductive effect. This can be understood since again the powers of $\mathcal{E}$ decrease strongly with increasing n_s, while all the non-vanishing δq_s terms are roughly of the same order of magnitude.

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(17) Terms in δp_{rs} were neglected, *cf.* above.

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Infrared Studies of the Association of Secondary Amides in Various Solvents

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The infrared spectra of N-ethylacetamide, N-*n*-butylacetamide and γ-butyrolactam have been measured in the regions 3500 to 3000 cm.$^{-1}$ and 1700 to 1600 cm.$^{-1}$ as a function of concentration in carbon tetrachloride, and as a function of solvent at fixed concentration. Significant spectral changes are observed with seemingly similar solvents. It is suggested that changes in the spectrum are caused primarily by variation of the polymerization constant with solvent. Evidence is presented for weak hydrogen bond formation between chloroform and the carbonyl group of the amide.

The association of amides has been well known for a number of years[1] and much infrared spectral study[2,3] has been devoted to these compounds. Yet the conditions under which dimeric association, rather than higher polymerization, occurs are not well known. It has been clearly shown that the functional groups responsible for the association are the amino and the carbonyl groups by formation of NH–OC bonds.[3] Beyond this point the situation is less clear. For primary amides there is considerable evidence of polymers higher than dimers.[1,4,5] It has been suggested that secondary amides associate in cyclic dimers, as do the carboxylic acids, and consequently dimeric units should be favored over higher polymers.[6] In apparent support of this suggestion are the studies of δ-valerolactam,[7-9] where only dimeric units were found. In conflict with this suggestion is the definitive work of Mizushima, *et al.*,[10] on N-methylacetamide in carbon tetrachloride solutions. The high dielectric constant indicates chain polymers, and the frequency shift of the bonded NH absorption with concentration shows existence of several species.

In addition to consideration of the polymeric species resulting from hydrogen bonding, the present work includes study of the influence of several solvents, usually considered to be intercomparable, upon the spectra of the amides. This appeared important in view of previous work[3] which showed that oxygenated solvents have large effects upon amides not explainable in terms of the dielectric constants of the solvents.

Experimental

A Perkin-Elmer Model 21 infrared spectrometer was used to obtain the spectrograms. The spectra of the amides in carbon tetrachloride as a function of concentration were obtained with NaCl optics. The spectra of N-ethylacetamide in different solvents were obtained with a CaF_2 prism. For NaCl optics frequency accuracy is estimated as 25 cm.$^{-1}$ at 3000 cm.$^{-1}$ and 7 cm.$^{-1}$ at 1700 cm.$^{-1}$. For CaF_2 optics the accuracy is higher, namely, 10 cm.$^{-1}$ at 3000 cm.$^{-1}$ and 3 cm.$^{-1}$ at 1700 cm.$^{-1}$. In each region, frequency reproducibility is better than the absolute accuracies quoted above. Cell lengths are shown in the tables.

Results and Discussion

The results of measurements in carbon tetrachloride as a function of amide concentration are presented in Table I. In all cases the location of the absorption maximum ν, and the apparent molal extinction coefficient e of the absorption maximum have been corrected for overlapping absorption by the wings of neighboring bands. Frequency and intensity reproducibility were checked by the CH absorption. The apparent molal extinction coefficient refers to stoichiometric concentration. The units are moles^{-1} cm.^{2}, and it is computed from absorption measurements, using $\log_{10} I_0/I$ at the absorption maximum.

The data in Table I strongly support the hypothesis that the only polymeric species in carbon tetrachloride solutions of butyrolactam is a cyclic dimer.

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(1) E. N. Lassettre, *Chem. Revs.*, **20**, 259 (1937).

(2) (a) A. M. Buswell, W. H. Rodebush and M. F. Roy, THIS JOURNAL, **60**, 2444 (1938); (b) H. Lenormant, *Ann. Chim.*, **5**, 459 (1950).

(3) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

(4) M. J. Copley, G. F. Zellhoefer and C. S. Marvel, THIS JOURNAL, **60**, 2666 (1938).

(5) M. Davies and H. E. Hallem, *Trans. Faraday Soc.*, **47**, 1170 (1951).

(6) H. Letaw, Jr., and A. H. Gropp, *J. Chem. Phys.*, **21**, 1621 (1953). (Reference is given therein to earlier work.)

(7) M. Tsuboi, *Bull. Chem. Soc. Japan*, **22**, 215 (1949).

(8) M. Tsuboi, *ibid.*, **24**, 75 (1951).

(9) G. I. Jenkins and T. W. J. Taylor, *J. Chem. Soc.*, 495 (1937).

(10) S. Mizushima, T. Simanouti, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, THIS JOURNAL, **72**, 3490 (1950).