requirements should be analyzed by calculation of R and $\bar{\sigma}_R$-values ($R = \log (k/k_0) - \sigma_I\rho$; $\bar{\sigma}_R = R/\rho$). Correlation of these resonance parameters with corresponding values for potentially similar reaction processes may then be attempted. Several alternate (but not necessarily equivalent) procedures may be used in attempting these correlations. The values of $\bar{\sigma}_R$ for the reaction series of interest may be compared directly with corresponding $\bar{\sigma}_R$-values for reaction series which are expected to be of the same reactivity category. If the values agree for a wide variety of substituents for two or more pairs of reaction series within the precision indicated above, a precise correlation of the unique resonance effects is demonstrated. Alternately, the corresponding values of R in two reaction series may be plotted one *vs.* the other to determine if a precise correlation of the resonance effects exists. Finally, if the reaction series of interest is expected by its nature to show resonance effects closely related to those for a limited reactivity category which has been previously demonstrated to show (within the category) generalized resonance effects which are precisely correlated by a characteristic set of resonance parameters (as, for example, the σ_R^0-values discussed in paper VI),[11] a plot of the R values *vs.* these resonance parameters (σ_R^0, for example) may be made. A satisfactorily precise correlation should be judged by the same precision criterion given above for σ^m-values. Examples of the utility of plots of R-values *vs.* σ_R^0-parameters are discussed in paper VI of this series.[11]

The establishment of precise linear correlations between unique resonance effects in closely related reactivities offers a major tool in the determination of the properties of transition states in reaction mechanism studies. Similar correlations for equilibria provide valuable information on the nature of resonance interactions. It is the very appreciable dependence of the precise order of resonance effects of substituents on the reactivity type and conditions which makes these correlations of especial utility.

The modification we here propose is in no way intended to discredit the many useful purposes for which the original form of the Hammett equation serves quite adequately.[5,6,14] Our purpose is to provide a soundly based procedure which may be used by investigators whose intent is to obtain a more intimate understanding of the effects of structure on reactivity than is permitted by the relationship in its original form.

University Park, Penna.

[Contribution from the College of Chemistry and Physics, the Pennsylvania State University]

Evaluation of Resonance Effects on Reactivity by Application of the Linear Inductive Energy Relationship.[1,2] VI. Concerning the Effects of Polarization and Conjugation on the Mesomeric Order

By Robert W. Taft, Jr.,[3] Stanton Ehrenson,[4] Irwin C. Lewis and Richard E. Glick

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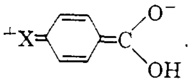
Results from reactivity analysis are reported which show the quantitative mesomeric order of $-R$ substituents in benzene derivatives can be strongly affected by polarization by the functional group. By consideration of resonance effects (R-values) of $-R$ *p*-substituents in reactivities in which conjugation with and/or strong polarization by the reaction center is precluded in either state of the reactivity, a precise quantitative scale of the power of mesomeric charge delocalization by $-R$ substituents is derived. Evidence is presented indicating that so long as the basic requirements for applicability of this σ_R^0 scale are met, the scale holds widely independent of reaction type or conditions. By means of the σ_R^0 scale it is shown that the effects of *p*-substituents, such as NH_2, OCH_3, etc., on the ionization of aqueous benzoic acids include important electromeric contributions. The difference $\bar{\sigma}_R^p - \sigma_R^0$ (where $\bar{\sigma}_R^p$ is the specific resonance parameter for the ionization of benzoic acids in water) is the contribution to the Hammett σ-value resulting from the isovalent conjugation (canonical) form:



. The shielding parameters (chemical shifts) for an extensive series of *m*- and *p*-substituents in the n.m.r. spectra of fluorobenzenes in dilute carbon tetrachloride solution have been determined. The results correspond closely to those obtained originally by Gutowsky in mixed liquid fluorocarbons. For *m*-substituents, the relationship, $\delta_m^F = 0.61\ \sigma_I - 0.05$, is followed to high precision (av. dev. = ± 0.035). *para* $-R$ substituents follow the relationship, $\delta_p^F = 0.90\ \sigma_I + 3.06\ \sigma_R^0 - 0.08$, to the same precision. The latter correlation corroborates the conclusions reached concerning the σ_R^0 scale of resonance effects. *para* $+R$ substituents give δ_p^F values with enhanced resonance contributions which are solvent dependent. Application of the σ_R^0 scale for estimation of special resonance and polarization effects in reactivities and physical properties is illustrated.

In previous papers of this series it has been shown that the effects of uncharged *m*- and *p*-substituents on the reactivities (log (k/k_0) values) of benzene derivatives may be treated as the sum of inductive and resonance parameters, I and R values, respectively.[2] The I-values follow with great generality and relatively high precision the Hammett-like linear inductive energy relationship,[5] $I = \sigma_I\rho$ (the ρ value used throughout the present papers refers to that obtained by the procedure proposed in ref. 2).

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[1] This work was supported in part by the Office of Naval Research, Project NR055-328. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] Paper V, R. W. Taft, Jr., and I. C. Lewis, This Journal, **81**, 5343 (1959). Paper V should be consulted for references to the earlier literature.

[3] (a) Alfred P. Sloan Fellow, 1955–1957; (b) John Simon Guggenheim Fellow, Harvard University, Fall term, 1958.

[4] Alfred P. Sloan Postdoctoral Fellow, 1956–1958.

[5] R. W. Taft, Jr., and I. C. Lewis, This Journal, **80**, 2436 (1958).

On the other hand, precise linear correlations of R-values are much more highly dependent upon reaction type and conditions.[2] The only precise correlations of R-values ($R^m = \rho\sigma_R^m$) which approach the generality of the inductive effect correlations are those for a select group of m-substituents. These correlations have been explained on the basis that the effects of the resonance interaction of the m-substituents are inductively transmitted through the bond (or space) between the benzene ring and the side-chain reaction center.[2] Consequently, the quantitative order of R-values for m-substituents is not affected by direct resonance interactions with the side chain reaction centers. Further, there is very little if any susceptibility of the effects of resonance interaction of the select group of m-substituents to the indirect polarizations afforded by the side-chain reaction centers. As a consequence, the observed effects of these substituents follow the Hammett equation, $\log(k^m/k_0) = \sigma^m\rho = (\sigma_I + \sigma_R^m)\rho$ with unusually high precision and generality.[2]

In the present paper additional results from the evaluation of R-values are reported. Reactivity evidence is presented which further supports the classical notion that no appreciable direct resonance interaction occurs from the m-position.[6] Evidence that the mesomeric order of certain substituents is affected by highly polarizing functional groups is given and discussed. A precise quantitative scale (σ_R^0 values) of the power of mesomeric charge delocalization of $-R$ substituent groups is derived. This scale is thought to be applicable for any unconjugated p-disubstituted benzene possessing in both states of the reactivity a functional group which is weakly polarizing. It is demonstrated that specific resonance and polarization effects of p-substituents may be identified by deviations from the relationship $R = \sigma_R^0\rho$(or $\log(k/k_0) = \sigma^0\rho$).

The resonance contributions to the shielding parameters of $-R$ (electron donating) m- and p-substituents in the nuclear magnetic resonance spectra of fluorobenzenes provide an important test of the σ_R^0 scale. These "chemical shifts" for F^{19} were initially obtained by Gutowsky, *et al.*,[7] in mixed liquid fluorobenzenes. We have reexamined the shielding parameters in very dilute carbon tetrachloride solution to eliminate the possibility of specific medium effects. Our new results (for $-R$ substituents) correspond very closely to those obtained originally by Gutowsky, *et al.* The results for $+R$ (acceptor) p-substituents show distinct solvent effects, as does the σ_R^0 scale for these substituents. These solvent effects will be the subject of a subsequent paper.

Results

R-Values of Opposite Sign in the m- and p-Positions.—Several reaction series have been found in which the R-values for corresponding substituents in the m- and p-positions are opposite in sign. These results are summarized in Table I in which the value of the specific resonance parameter, $\bar{\sigma}_R$, is listed for each substituent. The $\bar{\sigma}_R$ values (defined as $\bar{\sigma}_R \equiv R/\rho$ and which, therefore, refer to the resonance effect in a specific reaction) have proved extremely useful for examining correlations of R-values.[2]

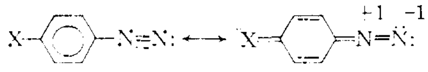
TABLE I

REACTION SERIES WITH $\bar{\sigma}_R$-VALUES OF OPPOSITE SIGN IN THE m- AND p-POSITIONS[a]

Reaction	B-13		E-4		E-8	
Subst.	$\bar{\sigma}_R^p$	$\bar{\sigma}_R^m$	$\bar{\sigma}_R^p$	$\bar{\sigma}_R^m$	$\bar{\sigma}_R^p$	$\bar{\sigma}_R^m$
CH_3O	−0.36	....	+0.62	−0.44	+1.23	−0.18
CH_3	− .14	.00	+ .27	− .11	+0.33	.00
Cl	− .14	+ .08	+ .18	− .14	− .43	− .33
Br	− .14	+ .08	....	....	....	....
C_6H_5	....	....	+ .21	− .19	....	....
NO_2	+ .06	− .02	− .06	+ .09	− .30	+ .07

[a] For a description of the reactions and literature references *cf.* Table II, paper V, ref. 2.

The directional dependence of these $\bar{\sigma}_R$ values supports the classical notion that there is little or no direct conjugation from the m-position. Such a condition leads directly to the possibility that the indirect resonance effect from the m-position may act to favor one state of the observed process whereas the direct resonance interaction produces the opposite order of stabilization on the two states involved. For example, in the decomposition of benzenediazonium salts in aqueous solution (reaction E-4, of Table I), inductive electron-release favors the transition state (phenyl cation in character) compared to the diazonium salt ($\rho = \rho_I = -4.21$). Consequently, *if no appreciable direct resonance interaction occurs between the meta $-R$ substituents and the N_2^+ side chain*, $-R$ substituents will accelerate the rate by the inductively transmitted charge donating effect ($\bar{\sigma}_R^m$ values will be negative as usual) as is observed.[8] On the other hand, the diazonium salts are strongly stabilized by $-R$ p-substituents through isovalent[9] conjugation of the type



Such a resonance stabilization is presumably substantially if not entirely lost in the decomposition transition state ($Ar^+ \ldots N_2$), so that the effect of direct conjugation of the p-substituent with the side chain functional group is to decrease the reaction rate.[8] If this effect predominates it becomes formally apparent by a change in the usual sign of the $\bar{\sigma}_R$-value for the *para* $-R$ substituent, as is obtained in a very pronounced manner for this reaction. A similar explanation may account for the directional character of the $\bar{\sigma}_R$-parameters for the OCH_3 substituent in the rates of formation of benzaldehyde semicarbazones (reaction E-8).[10] The opposite signs of corresponding $\bar{\sigma}_R^m$ and $\bar{\sigma}_R^p$-values in the methoxide-catalyzed deacetylation

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(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VI.

(7) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952); (b) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(8) J. F. Bunnett and E. Zahler, *Chem. Revs.*, **49**, 273 (1951); E. S. Lewis and E. B. Miller, THIS JOURNAL, **75**, 429 (1953).

(9) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

(10) This interpretation of these data is made uncertain, however, by the possibility that for the complex semicarbazide reaction, the same rate-determining step may not pertain for all substituents; *cf.* D. S. Noyce, A. T. Bottini and S. G. Smith, *J. Org. Chem.*, **23**, 752 (1958).

of 2-NO_2-1-acetanilides (reaction B-13) may be attributed to the direct resonance interactions of the *m*-substituents with the 2-nitro group.[11] White, *et al.*,[12] have reported a further interesting example in which the direction of resonance effects of *m*-substituents is opposite to that for *p*-substituents.

Polarization of Mesomeric Charge-release by Functional Centers.—The $\bar{\sigma}_R{}^m$-values obtained for the *m*-substituents NH_2 and $N(CH_3)_2$ (and apparently to a lesser extent CH_3S) reveal a dependence on reaction type of such magnitude that these substituents cannot be included in the σ_R-scale of resonance effects (the standard deviation for the average value greatly exceeds $\pm 0.03^2$). An examination of the results shows a systematic relationship exists between the reactivity type and the $\bar{\sigma}_R{}^m$-parameters. Tables II and III summarize all of the available $\bar{\sigma}_R{}^m$-values for these substituents.[2] In Table II are listed the reaction series which give $\bar{\sigma}_R{}^m$-values conforming to a precise mean value. The precision is of the same order ($S = \pm 0.03$) as for the $\sigma_R{}^m$-scale. Table II includes reactions in which the reaction conditions have been widely varied as indicated by the ranges of solvents and temperatures recorded in the table. The reactivity types giving this high degree of conformity appear to bear in common reaction centers (in both states of the reaction process) which are not highly polarizing. Thus reactions A.1, A.2, A.10, A.13 are benzoic acid ionizations. Reactions A.15, A.16 and A.24 are benzoate saponification rates and A.19 is the saponification of cinnamate esters; B-6 is the second ionization of phenyl phosphonic acids; E-2 is the equilibrium

TABLE II

$\bar{\sigma}_R{}^m$-VALUES[a]

Reaction	Solvent	Temp., °C.	NH_2	$N(CH_3)_2$	SCH_3
A.1	H_2O	25	−0.26	−0.25	−0.10
A.2	50% aq. ethanol	25	− .23	....	− .12
A.10	Ethanol	25	− .25	....	....
A.13	Benzene	25	− .25	− .26	....
A.15	60% aq. acetone	25	− .20	− .25	− .13
A.16	88% aq. ethanol	30	− .25	....	....
A.19	88% aq. ethanol	30	− .26	....	....
A.24	15% aq. ethanol	25	− .24	....	....
B.6	H_2O	25	− .18	....	....
E.2	$(CH_2OH)_2$	197	− .29	....	....
		Average $\bar{\sigma}_R{}^m$	− .24	− .25	− .12
		Standard error	.03	.01	.02

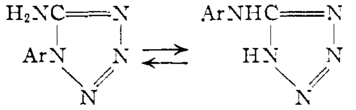
[a] For a description of the reactions and literature references *cf*. Table II, paper V, ref. 2.

TABLE III

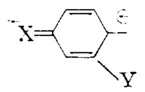
$\bar{\sigma}_R{}^m$ VALUES[a]

Reaction	Solvent	Temp., °C.	NH_2	$N(CH_3)_2$	SCH_3
B.7	25% aq. ethanol	25	−0.07	....	....
C.1	H_2O	25	− .06	−0.06	−0.03
C.4	48% aq. ethanol	25	....	− .17	....
C.9	H_2O	25	− .13	....	− .06
D.3	90% aq. acetone	25	....	....	− .09
D.12	Nitromethane	30	...	....	− .07
E.1	H_2O	25	− .42	....	....
E.3	H_2O	25	− .75	....	....

[a] For a description of the reactions and literature references *cf*. Table II, paper V, ref. 2.



None of these reactions involves a reaction center in which the first atom of the side chain bears a formal charge. Further the functional centers (in either state) in all of these reactions have Hammett σ-values (as substituent groups) which fall in the range ± 0.4. It is thus reasonable that the benzene system is not highly polarized in any state of these reactions by the functional center, Y, and the fractional contributions to the resonance hybrid of the v.b. structures, *e.g.*



are essentially the same for the substituents (X) of Table II for all of the benzene derivatives and reaction conditions listed.[2]

Table III lists $\bar{\sigma}_R{}^m$-values for the NH_2, $N(CH_3)_2$ and SCH_3 groups for reaction series which do not conform to the mean values of Table II. The non-conformity is indeed great for the amine substituents. The range in $\bar{\sigma}_R{}^m$-values for the NH_2 group covers better than a twelve-fold variation. In none of these reactions can the variation be attributed to protonation of the amino substituent. All of the reactions of Table III have in common the feature that the *first atom of the side chain functional group bears a formal charge* in one state of the reaction process. The reactions of Table III are

$$\text{B.7, } ArB(OH)_2 \underset{}{\overset{+H_2O}{\rightleftharpoons}} Ar\overset{\ominus}{B}(OH)_3 + H^+;$$

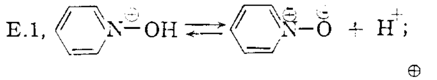
$$\text{C.1, } ArOH \rightleftharpoons Ar\overset{\ominus}{O} + H^+;\ \text{C.4, } ArSH \rightleftharpoons Ar\overset{\ominus}{S} + H^+;$$

$$\text{C.9, } Ar\overset{\ominus}{N}H_3 \rightleftharpoons ArNH_2 + H^+;$$

$$\text{D.3, } Ar(CH_3)_2C\text{–}Cl \longrightarrow Ar\overset{\ominus}{C}(CH_3)_2 + Cl^-;$$

$$\text{D.12, } ArSi(CH_3)_3 + H^+ \longrightarrow \overset{\oplus}{Ar}HSi(CH_3)_3;$$

E.1,



$$\text{E.2, } ArNH_2 \longrightarrow Ar\overset{\oplus}{N}H_2 + e$$

We believe these results provide conclusive evidence that the order of mesomeric electron release, even if restricted to charge delocalization within the benzene ring alone, can be strongly affected by polarization by the functional group.

Although the *m*-methoxy substituent shows a high degree of conformity to the σ_R-scale[2] ($\sigma_R{}^m = -0.19$), substantially enhanced $\bar{\sigma}_R{}^m$ values are obtained for this substituent (and other $-R$ substituents) in reactions E-3 and E-4 (see Table I)

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(11) B. M. Wepster and P. E. Verkade, *Rec. trav. chim.*, **68**, 77, 88 (1949).

(12) W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, This Journal, **80**, 3271 (1958); *cf.* also H. L. Goering and R. R. Jacobsen, *ibid.*, **80**, 3285 (1958).

TABLE IV

THE $\sigma_R{}^{\circ}$-SCALE[a]

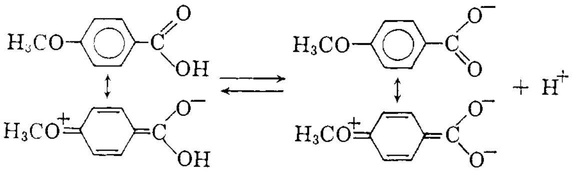
Reaction Solvent p-Substituent	B.1 pK_a $ArCH_2$-CO_2H H_2O	B.2 Saponification $ArCH_2$-CO_2Et 88% aq. C_2H_5OH	B.14 Saponification $ArCH_2$-$OCOCH_3$ 60% aq. acetone	$2.0\sigma_R{}^m$	A.13 Ion-pair formation $ArCO_2H$ Benzene	ν_{OH} $ArCO_2H$[e] CCl_4	B.6 pK_a $ArPO_2OH^-$ H_2O	A.1 pK_a $ArCO_2H$ H_2O	$\sigma_R{}^0$
$N(CH_3)_2$				−0.50[b]		−0.54		−0.82[f]	−0.54
NH_2		−0.48		− .48[b]	−0.46	− .43	−0.49	− .76	− .48
$NHCOCH_3$				− .20[c]	− .28[d]		− .30	− .28	− .25
OCH_3	−0.39	− .38	−0.42	− .38	− .40	− .42		− .56	− .41
OH					− .39	− .36	− .40	− .62	− .40
SCH_3				− .24[b]	− .25[d]			− .25	.24
F	− .39		− .35	− .34	− .36			− .46	− .35
Cl	− .22	− .15	− .19	− .20	− .22	− .24	− .20	− .24	− .20
Br	− .20		− .20	− .14	− .18		− .25	− .22	− .19
I	− .11		− .12	− .08	− .13			− .12[f]	− .12
C_6H_5				− .08[d]	− .11[d]			− .11	− .10
CH_3	− .09	− .08	− .13	− .06	− .05		− .09	− .12	− .10
H	.00	.00	.00	.00	.00	.00	.00	.00	.00

[a] For a description of the reactions and literature references *cf.* Table II, paper V, ref. 2. Values listed in this table, unless otherwise designated, are the $\bar{\sigma}_R{}^p$-value obtained for these reactions. [b] Based upon average of $\bar{\sigma}_R{}^m$, Table II. [c] Based upon average of $\bar{\sigma}_R{}^m$-values for reactions A.1 and A.24, Table II, ref. 2. [d] Based on $\bar{\sigma}_R$-values for reaction A.1, Table II, ref. 2. [e] Based upon data of J. Goulden, *Spectrochim. Acta*, **6**, 129 (1954). The values of $\bar{\sigma}_R{}^p$ are obtained as follows: $\bar{\sigma}_R{}^p = (1/19.0)[\Delta\nu_{obs} - (11.7)\sigma_I]$ where $\Delta\nu_{obs}$ is the frequency shift relative to benzoic acid (in cm.$^{-1}$). The value of $\rho_I = 11.7$ was obtained by the use of equation 5 of ref. 2 making use of $\Delta\nu$-values for corresponding *m*- and *p*-substituents. [f] $\bar{\sigma}_R{}^p$-values for reaction A.15, Table II, ref. 2.

which involve phenyl cation reactivities. In the radical reactions F-1, F-3 and F-4 enhanced $\bar{\sigma}_R{}^m$-values of the same magnitude also apply for the *m*-methoxy substituent.

The $\sigma_R{}^0$-Scale.—In addition to polarization by the functional centers, the resonance parameters for *p*-substituents may be affected by direct conjugation between the substituent and the reaction center. It has been well established that enhanced resonance effects are obtained for $-R$ *p*-substituents in electrophilic reactivities and for $+R$ *p*-substituents in nucleophilic reactivities.[13]

It has been suspected too, for example, that the Hammett σ-value (and therefore the $\bar{\sigma}_R{}^p$-value) for the *p*-methoxy group includes a contribution resulting from a change between benzoic acid and benzoate ion in the direct isovalent conjugation[14]



We find that $\bar{\sigma}_R{}^p$-values for the *p*-methoxy group (as well as for other strong $-R$ substituents) are widely variant. Even if reactivities in the electrophilic (D), amphoteric (E) and radical (F) categories[2] are excluded, the $\bar{\sigma}_R{}^p$-value still shows a range from -0.30 to -0.64 with a high population of values over this whole region. Consequently, we conclude that the resonance effects (*R*-values) for the *p*-methoxy group are appreciably affected by direct conjugation with and/or polarization by the functional groups.

Although no σ_R-scale of resonance effects (precise to ±0.03) can be applied with a high degree of generality to any *p*-substituent,[2] it is of interest and great usefulness to determine whether a common precise scale of mesomeric orders exists for *p*-substituents in derivatives of benzene for which direct resonance interaction with the reaction centers is precluded and for which relatively little polarization is exerted by the functional groups. Examination of appropriate *R* (and $\bar{\sigma}_R{}^p$) values discloses that such a scale does exist. In Table IV are collected $\bar{\sigma}_R{}^p$-values for three reaction series of the $ArCH_2Y$ type, reactions B.1, B.2 and B.14. Direct resonance interactions between the *p*-substituent and the functional group, Y, or polarization by a formal charge on the first atom of the side chain are precluded by the nature of this system. Table IV illustrates the close conformity shown by $\bar{\sigma}_R{}^p$-values for all reactivities of the $ArCH_2Y$ type. Table IV further illustrates the precise correlation between these $\bar{\sigma}_R{}^p$-values and corresponding values[2] of $\sigma_R{}^m$ (using for NH_2, $N(CH_3)_2$ and SCH_3 substituents, the $\bar{\sigma}_R{}^m$-values of Table II), *i.e.*, $\bar{\sigma}_R{}^p = 2.0\sigma_R{}^m$. This precise correlation is expected on the basis that neither the $\bar{\sigma}_R{}^p$-values from $ArCH_2Y$ reactivities or the $\sigma_R{}^m$-values are measurably affected by direct conjugation and functional group polarization effects. It is of further interest to note that this correlation meets Hine's criterion of generality of σ-values.[15] Further illustrated in Table IV are two additional reaction series (A.13, B.6) and a series of OH vibrational frequencies in *p*-substituted benzoic acids which give $\bar{\sigma}_R{}^p$-values which closely conform to those obtained from the $ArCH_2Y$ reactivities.

The striking success of these correlations leads us to propose a quantitative order of mesomeric donor power for $-R$ substituents, the $\sigma_R{}^0$-scale, applicable to any derivative of benzene possessing

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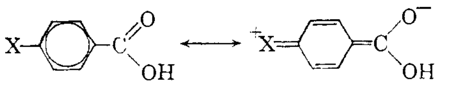
(13) For a review and references to this subject *cf.* R. W. Taft, Jr., N. C. Deno and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 287 (1958).

(14) (a) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 246–257, 416–419; (b) F. G. Bordwell and P. J. Boutan, THIS JOURNAL, **78**, 854 (1956); **79**, 719 (1957).

(15) J. Hine, *ibid*, **81**, 1126 (1959).

in both states of the reactivity a weakly polarizing non-conjugated (with the *p*-substituent) functional group. Values of σ_R^0 are listed in Table IV. The precision of these parameters is clearly comparable to that of the σ_R^m-scale ($S = \pm 0.03$).[2] It appears from the rather diverse nature of the reaction series on which the σ_R^0-scale is based that these parameters apply independent of whether the process is a reaction rate or equilibrium, the nature of the solvent, and the nature of the reactivity type, provided that the basic conditions for applicability of this scale are met.

Listed for comparison with σ_R^0-values are the $\bar{\sigma}_R^p$-values for the ionization of benzoic acids in water at 25°, *i.e.*, the resonance parameters derived from Hammett σ-values. While it is clear that both sets of resonance parameters correspond to Ingold's mesomeric order,[6] it is equally apparent that the two scales are quantitatively distinct. Thus the corresponding resonance parameters for the weakly donating groups (*e.g.*, C_6H_6, I, Br, Cl, SCH_3 and $NHCOCH_3$) have nearly equivalent values. On the other hand, the stronger donating groups (F, OH, OCH_3, NH_2 and NMe_2) have distinctly enhanced resonance effects in the ionization of benzoic acids in water. The $\bar{\sigma}_R^p$-values for $N(CH_3)_2$, for example, is about 60% greater than the σ_R^0-value. The enhancements ($\Delta = \bar{\sigma}_R^p - \sigma_R^0$) are the effects on Hammett σ-values (and $\bar{\sigma}_R^p$-values) resulting from the isovalent conjugation



The resonance effects resulting from such conjugations are strongly dependent upon the nature of the solvent as is clearly indicated by the conformity of the highly valuable data of Davis and Hetzer[16] for ion-pair formation between benzoic acids and 1,3-diphenylguanidine in benzene solution (reaction A.13) to the σ_R^0-scale. The role of solvent assisted mesomeric charge separation on reactivity effects is considered in detail in a subsequent paper of this series. No σ_R^0-values are listed in Table IV for +R *p*-substituents (*e.g.*, NO_2, etc.) since the resonance effects for such groups have a distinct solvent dependence and will be discussed in the above paper.

In addition to the reactivities listed in Table IV the σ_R^0-scale is followed by several substituents in a large number of reactivities. With few exceptions the $\bar{\sigma}_R^p$-values for the halogens (Cl, Br and I) and the methyl group in benzoic (A), miscellaneous (B), nucleophilic (C) reactivity categories follow the σ_R^0-scale within a range of ±0.07 units and with a standard error of ±0.03. To the same degree of precision, the *p*-methoxy group follows the σ_R^0-scale in the following reactivities (*cf.* Table II, ref. 2, for description): A-23, B-3, B-12, B-13, C-1, C-2, C-3, C-4, C-5, C-8, C-17 and C-18. The *p*-OH group shows frequent deviations from the σ_R^0-values, especially in certain reactivities in aqueous media where hydrogen bonding by this substituent is effective.[17]

σ-Values for *p*-substituents derived from the σ_R^0-scale may be given by the symbol σ^0, *i.e.*, $\sigma^0 = \sigma_R^0 + \sigma_I$. Values of σ^0 are listed in Table V. These σ^0-values are expected to apply according to the Hammett equation, $\log (k/k_0) = \rho\sigma^0$, to any reactivity of *p*-substituents for which there is no direct conjugation with the functional center (resonance with the ring only) and for which there is little or no polarization effect by the reaction centers in either state of the reactivity. All of the reactivities listed above, of course, follow the σ^0-scale to high precision.

Table V

σ^0-Values from the σ_R^0-Scale

Substituent	σ^0_{para}	Substituent	σ^0_{para}
$N(CH_3)_2$	−0.44	Cl	+0.27
NH_2	− .38	Br	+ .26
$NHCOCH_3$	+ .03	I	+ .27
OCH_3	− .12[a] − .16[b]	C_6H_5	.00
OH	− .15	CH_3	− .15
F	+ .17	H	.00

[a] Value for pure aqueous solutions, cf. ref. 2, footnote 12.
[b] Value for non-aqueous solutions.

Shielding Parameters for −*R* Substituents in the N.m.r. Spectra of ArF^{19}.—The chemical shifts of F^{19} in *m*- and *p*-substituted fluorobenzenes examined by Gutowsky, *et al.*,[7] have been reinvestigated in very dilute carbon tetrachloride solution. Gutowsky's general method employed approximately 50% by volume liquid mixtures of fluorobenzene and the substituted fluorobenzene. Our measurements have been carried out either (A) with an external standard using several known concentrations of the substituted fluorobenzene in carbon tetrachloride and extrapolation made to infinite dilution or (B) at low concentration (5%) of the substituted fluorobenzene and fluorobenzene (as the internal standard) in carbon tetrachloride solution. The results obtained by either procedure are closely similar (see Experimental methods A and B for particular procedures).

The shielding parameters, $\delta^F = 10^5 (H_{C_6H_5F} - H_{XC_6H_4F})/H_{C_6H_5F}$ of Gutowsky for *m*-substituents have been precisely correlated with the inductive parameters, σ_I.[18] The present investigation of *m*-substituents in dilute carbon tetrachloride solution gives virtually identical shielding parameters (*cf.* Table VI). The remarkably precise and general correlation (1) $\delta_m^F = 0.61\ \sigma_I - 0.05$, av. dev. = ± 0.03, has been recently summarized by Taft and Lewis.[19]

Table VI summarizes the values of the shielding parameters which we have obtained in carbon tetrachloride solution. Listed for comparison in Table VI are the values reported originally by Gutowsky, *et al.* It is apparent that our values in carbon tetrachloride differ in a minor way from Gutowsky's values in mixed liquid fluorobenzenes, indicating that the latter F^{19} shifts were not strongly affected by specific medium effects.

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(16) M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Stand.*, **60**, 569 (1958).

(17) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(18) R. W. Taft, Jr., This Journal, **79**, 1045 (1957).

(19) Reference 2, Table I.

TABLE VI

SHIELDING PARAMETERS FOR *m*- AND *p*-SUBSTITUTED FLUOROBENZENES

Substituent	CCl₄ solution[a]		Mixed fluorocarbon[b]	
	δ_{para}	δ_{meta}	δ_{para}	δ_{meta}
H	0.00	0.00	0.00	0.00
$N(CH_3)_2$	....	....	−1.68	....
NH_2	−1.41	+ .02	−1.46	−0.02
OCH_3	−1.15	+ .11	−1.14	+ .13
OH	−1.08	....	−1.06	+ .09
$NHCOCH_3$	....	+ .11	−0.57[c]	+ .10[c]
F	−0.68	+ .30	− .64	+ .31
Cl	− .32	+ .20	− .24	+ .21
Br	− .25	+ .22	− .23	+ .24
I	....	....	− .12	+ .26
C_6H_5	− .32	....	− .27[c]	+ .06
CH_3	− .54	− .12	− .55	− .09
CF_3	+ .51	+ .21	....	+ .28
CO_2Et	+ .61	....	....	....
$COCH_3$	+ .66	+ .11	....	....
CN	+ .94	....	+ .96	+ .30
CHO	+ .94	....	+ .98	+ .10
NO_2	+ .97	....	+1.08	+ .33

[a] Present investigation. [b] Work of reference 7. [c] Value obtained in ethanol solution.

While the shielding parameters for *m*-substituents are in the inductive order: $CH_3 < H < NH_2 < OH < Br < NO_2$, the parameters for *p*-substituents follow Ingold's mesomeric order[6]: $NH_2 < OH < F < CH_3 < H < NO_2$ (*cf.* Table VI). In addition, the *p*-shielding parameters are so much larger than the corresponding *m*-parameters that the quantity $\delta_p^F - \delta_m^F$ is an accurate resonance parameter, since the assumption of equal inductive contributions to corresponding δ_p^F and δ_m^F values, if not strictly correct, will introduce very little error.[7,18]

The $\delta_p^F - \delta_m^F$ values provide an interesting test of the σ_R^0-scale. Taft[18] has previously reported a reasonably precise correlation between Gutowsky's values of $\delta_p^F - \delta_m^F$ and $\bar{\sigma}_R^p$-values from the ionization of benzoic acids in water (*i.e.*, $\bar{\sigma}_R^p$-values from Hammett σ^p-values). Presumably $s_p^F - \delta_m^F$ values are quantitative measures of the effect of mesomeric charge delocalization by the *p*-substituent on the ionic character of the Ar–F bond[7,18,20] (a negative value indicates a decrease in the ionic character of the bond). For $-R$ *p*-substituents direct conjugation with the fluorine atom is precluded. Further, the fluorine atom is not expected to exert a strong polarizing influence on the benzene system. For example, a rather small net effect of mesomeric and inductive interactions by the fluorine atom is indicated by the small Hammett σ-value (+0.06) for the *p*-fluoro substituent. Consequently it is expected that $\delta_p^F - \delta_m^F$ values should be correlated by σ_R^0-values to greater precision than the earlier correlation with the $\bar{\sigma}_R^p$-values.

The precise correlation of $\delta_p^F - \delta_m^F$ values by σ_R^0-parameters according to the equation 2, $\delta_p^F - \delta_m^F = 2.97\sigma_R^0$ is indicated in Table VII by the comparison between calculated and observed values of $\delta_p^F - \delta_m^F$. The improved precision of this correlation over the original (eq. 3, $\delta_p^F - \delta_m^F = 1.88\bar{\sigma}_R^p - 0.06$) is illustrated in Table VII.

TABLE VII

CORRELATION OF SHIELDING PARAMETERS BY σ_R^0-VALUES

Substituent	$\delta_p^F - \delta_m^F$ exptl.	$\delta_p^F - \delta_m^F$ calcd. eq. 2	Dev.	$\delta_p^F - \delta_m^F$ calcd. eq. 3	Dev.
$N(CH_3)_2$	−1.69	−1.60	0.09	−1.60	0.09
NH_2	−1.43	−1.43	.00	−1.49	.06
$NHCOCH_3$	−0.68	−0.74	.06	−0.59	.09
OCH_3	−1.26	−1.22	.04	−1.11	.15
OH	−1.17	−1.19	.02	−1.23	.05
F	−0.97	−1.04	.07	−0.92	.05
Cl	− .51	−0.60	.09	− .51	.00
Br	− .47	− .57	.10	− .47	.00
I	− .38	− .36	.02	− .29	.09
C_6H_5	− .33	− .30	.03	− .27	.06
CH_3	− .42	− .30	.12	− .29	.13
H	.00	.00	.00	− .06	.06
		Av.	0.05	Av.	0.07

The high precision of equation 2 has prompted us to investigate the assumption of equal inductive contributions to δ_p-and δ_m-values. The δ_m-values follow with high precision the σ_I-inductive effect scale ($\delta_m = 0.61\sigma_I - 0.05$, av. dev. = 0.035). Consequently we may expect the inductive contribution to the δ_p-values to follow the σ_I-scale to the same order of precision, but the susceptibility factor, $\rho_I^m = 0.61$, need not necessarily be the same in the *p*-position. Accordingly we have examined the precision of the least squares best fit of δ_p^F-values to the equation 4: $\delta_p^F = \rho_I^p\sigma_I + \rho_R\,\sigma_R^0 + a$. The results are shown in Table VIII, which compares experimental δ_p^F-values with values calculated by equation 4 using the least squares parameters, $\rho_I^p = +0.90$, $\rho_R = +3.06$, $a = -0.08$.

TABLE VIII

CORRELATION OF *Para* SHIELDING PARAMETERS BY EQ. 4

Substituent	δ_p^F (exptl.)	δ_p^F calcd. eq. 3	Dev.
H	0.00	−0.08	0.08
$N(CH_3)_2$	−1.68	−1.64	.04
NH_2	−1.41	−1.46	.05
$NHCOCH_3$	−0.57	−0.59	.02
OCH_3	−1.15	−1.11	.04
OH	−1.08	−1.08	.00
F	−0.68	−0.68	.00
Cl	− .32	− .27	.05
Br	− .25	− .26	.01
I	− .12	− .10	.02
C_6H_5	− .32	− .30	.02
CH_3	− .54	− .43	.11
			Av. dev. = 0.035

The precision of eq. 4 is the same as that obtained in correlating by eq. 1 the δ_m^F-values with σ_I. The correlations by eq. 1 and 4 are as exact relationships as permitted by the combined uncertainties in δ_m-, δ_p-, σ_I- and σ_R^0-values. The results of equation 1 and 4 may be taken as providing some indication of a somewhat greater inductive contribution to the *para* than the *meta* shielding parameter, *i.e.*, $\rho_I^p/\rho_I^m = 0.90/0.61 = 1.5$. Such a result is in accord with Ingold's proposal of an alternating inductive effect.[6] It must be emphasized, however, that our evidence on this point is *by no means conclusive*. This is indicated by the only slightly poorer precision of equation 2

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(20) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(which assumes $\rho_I^p = \rho_I^m$) than equation 4. Reactivity analysis[21] has favored the conclusion that $\rho_I^p/\rho_I^m = 1.0$. To a rough approximation present results confirm this conclusion. To a finer approximation there is, of course, no requirement that the inductive effect ratio from the *m*- and *p*-positions need be the same for shielding parameters as for reactivities since the relative contributions of the field[22] and internal inductive[6] effects to these two observables need not be the same.

We believe that the precise correlation of δ_p^F-values by the σ_R^0-scale provides important evidence of the validity of these resonance parameters. Thus, although the evidence we have presented in an earlier section definitely supports the proposal of Corio and Dailey[23a] that quantitative mesomeric orders are subject to polarization effects by the functional group, we believe the evidence of the present and the previous sections indicates that the sensitivity to polarization is not nearly so great as these authors have suggested. In particular the conformance by $ArCH_2Y$ reactivities suggests that it is very likely that the σ_R^0-scale gives to good quantitative approximation the mesomeric order for monosubstituted benzenes. This conclusion is supported by the precise correlation of the proton nuclear magnetic resonance parameters, δ^H, for the most intense peak of monosubstituted benzenes: equation 5, $\delta^H = +0.040\ \sigma_I + 0.104\ \sigma_R^0 + 0.002$. The precision of equation 5 is illustrated in Table IX by comparison of calculated and experimental values. The precision of this correlation and the fact that the susceptibility factors ρ_I^H and ρ_R^H are in essentially the same ratio (1:2.6) as the corresponding factors for the *p*-substituted fluorobenzenes (1:3.4) appears to provide attractive empirical evidence that the most intense peak is correctly ascribed to the *p*-hydrogen atom. NOTE ADDED IN PROOF.—This identification has been verified for nitrobenzene by the comparison of the spectra of nitrobenzene and *p*-Dinitrobenzene, *cf.* J. A. Pople, W. G. Schneider, and H. S. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw Hill Book Co., New York, 1959, p. 258.

It is worthy of note that both $-R$ and $+R$ substituents have been correlated by equation 5, whereas conjugation between $+R$ *p*-substituents and the fluorine atom of fluorobenzene results in enhanced values of δ_p^F for the $+R$ substituents.[18] The σ_R^0-values used for the +R substituents in the correlation of Table IX are those appropriate to non-hydroxylic solvents (*e.g.*, CCl_4). The solvent dependence of δ_p^F-values and of σ_R^0-values for the $+R$ substituents will be discussed in a subsequent paper.

Use of the σ_R^0 Scale to Identify and Study Resonance and Polarization Effects.—Plots of R^p values *vs.* σ_R^0 and of R^m values *vs.* σ_R^m (or the equivalent of log (k^p/k_0) values *vs.* σ^0 and of log(k^m/k_0) values *vs.* σ^m) provide a valuable means for the determination of special resonance and/or polarization effects. An illustration of this method is provided by Fig. 1.

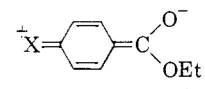
TABLE IX

CORRELATION OF PROTON SHIELDING PARAMETERS FOR SUBSTITUTED BENZENES BY EQ. 5[a,b]

Subst.	δ_H exptl. C. & D. in C_6H_{12}[23a]	δ_H exptl. B. & G. in CCl_4[23b]	δ_H calcd., eq. 5[c]
H	0.000	0.000	+0.002
$N(CH_3)_2$	− .050	.....	− .050
NH_2	− .040	.....	− .044
OH	− .037	.....	− .030
OCH_3	− .023	− .040	− .031
I	− .010	− .005	+ .005
Br	.000	+ .005	.000
Cl	.000	+ .002	.000
CH_3	− .010	− .018	− .010
CN	+ .030	+ .032	+ .030
$COCH_3$	+ .027	.....	+ .026
CO_2CH_3	+ .027	.....	+ .026
NO_2	+ .042	+ .045	+ .038

[a] Shielding parameters refer to those assigned for the highest proton resonance peak in the monosubstituted benzene. The parameters are obtained by the relationship, $\delta^H = 10^6 (H_{C_6H_6} - H_{XC_6H_5})/H_{C_6H_6}$. [b] Values of σ_R^0 employed for $-R$ substituents are those listed in Table IV. Unlike the substituted fluorobenzene system, $+R$ substituents can be included in this correlation due to the absence of isovalent conjugative interactions. The σ_R^0 values employed for these latter substituents are those to be reported in a subsequent paper. [c] The precision of this relationship is appreciably better than that obtained through correlation with Hammett σ-values or Brown σ^+-values.

Figure 1 shows *R*-values for the alkaline saponification rates of ethyl benzoates in 88% aqueous ethanol at 30° plotted *vs.* σ_R^0-values (for *m*-substituents, $\sigma_R^0 \equiv \sigma_R^m \cong \sigma_R^0\ para/2.0$). A precise linear plot results for all *m*-substituents (closed points), and the relationship includes a number of *p*-substituents (open circles). However, the $-R$ *p*-substituents SCH_3, F, OCH_3 and NH_2 deviate by progressively larger amounts (in the direction of slower reaction rates than expected for a non-conjugated substituent). The deviations not only provide a quantitative estimation of conjugation effects on the saponification rates but further the stabilization conferred upon the resonance hybrid of the *p*-substituted benzoates by the contribution of the isovalent resonance form



This conclusion follows from the evidence[24] that the transition state for the saponification reaction is essentially saturated at the carbonyl carbon (by OH^- addition) and consequently there is negligible stabilization of the transition state by a resonance form such as that above. The deviation of the *R*-values in Fig. 1 (*i.e.*, $R - \sigma_R^0\rho$) is therefore attributable to the additional resonance stabilization of the ester provided by the isovalent resonance structure.

In Table X are collected values of the estimated extra resonance energy of the benzoate esters,

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[21] *Cf.* ref. 2, footnote 9; compare, however, ref. 15.

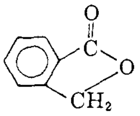
[22] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

[23] (a) P. L. Corio and B. P. Dailey, THIS JOURNAL, **78**, 3043 (1956); (b) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

[24] (a) M. L. Bender, THIS JOURNAL, **73**, 1626 (1951); (b) R. W. Taft, Jr., in M. S. Newman "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 588.

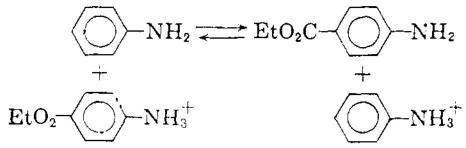
ΔE_ψ, obtained from the average deviations of the kind illustrated in Fig. 1 for reactions A.15 and A.16 of Table II, ref. 2 (rates of saponification of benzoates), reaction A.19 (saponification rates of cinnamate esters) and reaction A.24 (saponification rate of substituted phthalides), *i.e.*, $-2.303\ RT(\Delta R) \cong \Delta E_\psi$. Also listed in Table X are estimates of the contribution of the dipolar isovalent resonance form to the dipole moment and carbonyl vibration frequency. The former are values obtained by Rogers.[25] The latter were obtained from the data of Thomspon, *et al.*,[26] by applying the method illustrated by Fig. 1.

It is apparent from Table X that the extra resonance energies are approximately 40% greater for benzoate than corresponding cinnamate esters. Several factors may be involved, including some twisting from coplanarity of the phenyl and $CH{=}CHCO_2Et$ systems, an inherent resistance of the Ar–CH bond toward double bond formation, and the greater distance of separation of charge in the dipolar isovalent resonance form of the cinnamate. Evidence that the first factor does play a role is provided by the results for the five-membered ring lactone

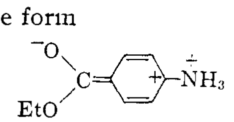


in which the carbonyl group is undoubtedly constrained to lie near coplanarity. The extra resonance energies for the lactones are about 15% greater than the corresponding values for the benzoates.

The extra resonance energy for the p-aminobenzoate given in Table X may be checked by considering the effect of the p-carboethoxy group as a substituent in the ionization of anilinium ions (reaction C-9). From the value of $\Delta R = R^p - \sigma_R{}^0\rho = 0.84$, one obtains for $\Delta E\psi$ the value 1.15 kcal./mole. The agreement may be considered fair, although the value in Table X is probably the better estimate. This conclusion follows from a consideration of the equilibrium



The position of this equilibrium (which is the measured effect of the EtO_2C group on the ionization of anilinium ion) depends not only on the resonance stabilization of the p-aminobenzoate but also on that for the substituted anilinium ion. Inasmuch as the resonance form



violates the adjacent charge rule, the substituted anilinium ion is destabilized with respect to ethyl benzoate. The difference in the above value of $\Delta E\psi$ and that given in Table X (0.25 kcal./mole) is probably a reasonable estimate of this destabilization. Wepster has given the figure 0.2 kcal./mole for the destabilization in the analogous p-nitroanilinium ion.[27]

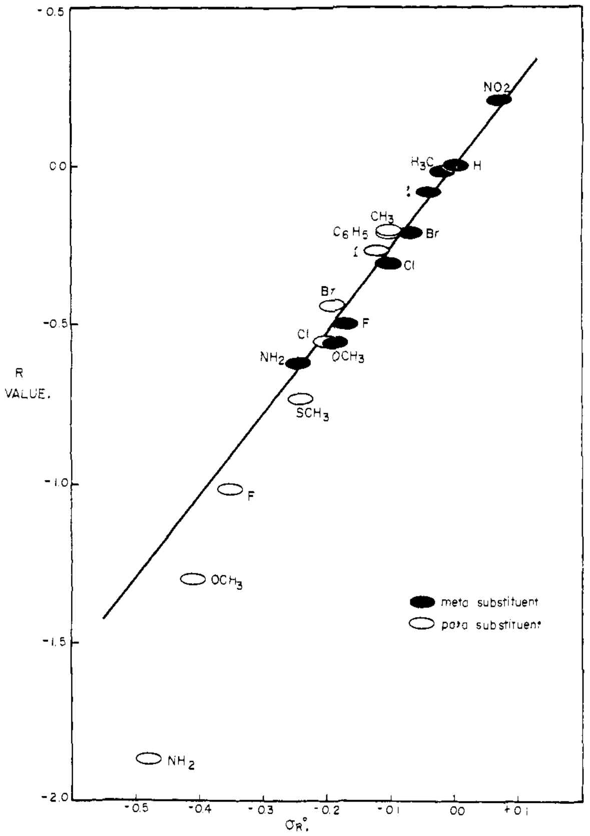
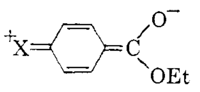


Fig. 1.—R-Values for the rates of saponification of ethyl benzoates, 88% aq. ethanol, 30°, plotted *vs.* $\sigma_R{}^0$ values. Closed circles are for m-substituents, open circles for p-substituents. Uncertainties in each $\sigma_R{}^0$-value of ±0.02 and in each R-value of ±0.04 have arbitrarily been used for illustration purposes.

TABLE X

CONTRIBUTIONS TO THE RESONANCE ENERGY, DIPOLE MOMENT AND CARBONYL STRETCHING FREQUENCY DUE TO THE DIPOLAR ISOVALENT RESONANCE FORM:



	Benzoate			Cinnamate	Phthalides
Solvent	$\Delta E\psi$, kcal. aq. organic solvents	$\Delta\mu$, D. dioxane	$\Delta\gamma$, cm.$^{-1}$ $CHCl_3$	$\Delta E\psi$, kcal. 88% aq. ethanol	$\Delta E\psi$, kcal. 15% aq. ethanol
$N(CH_3)_2$	0.95	..	..	..	..
NH_2	.90	0.55	−12	0.65	1.00
OCH_3	.45	.19	− 5	.25	0.55
SCH_3	.20	..	..	..	..
F	.15	..	− 4	.10	..
H	.00	.00	0	.00	0.00

In Fig. 2 the R-values for the ionization of phenols are plotted *vs.* corresponding $\sigma_R{}^0$-values. Omitted from the plot are R^p-values for $+R$ groups,

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[25] M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

[26] H. W. Thompson, R. W. Needham and D. Jameson, *Spectrochim. Acta*, **9**, 208 (1957).

[27] J. Burgers, M. A. Hoefnagel, P E. Verkade, H. Visser and B. M. Wepster, *Rec. trav. chim.*, **77**, 510 (1958).

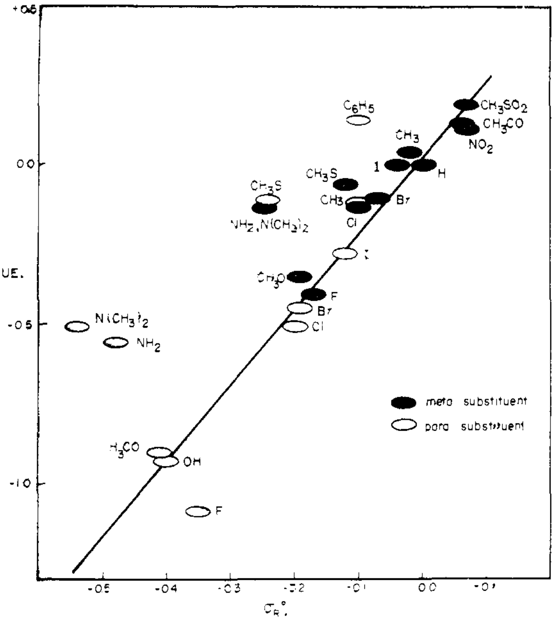
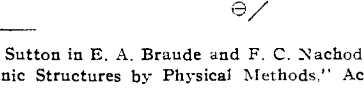


Fig. 2.—R-values for the ionization of phenols, H_2O, 25° plotted *vs.* σ_R^0-values. Closed circles are for m-substituents, open circles for p-substituents. Uncertainties in each σ_R^0-value of ± 0.02 and in each R-value of ± 0.04 have arbitrarily been used for illustration purposes.

which show substantial resonance enhancements.[13] The details of these deviations are considered in a subsequent paper. The important point for present purposes is that the deviations of the m-NH_2 and m-SCH_3 groups (as given in Table III) from the linear relationship followed by most of the m-substituents and several p-substituents are greatly magnified for the corresponding p-substituents. These polarization effects (direct resonance interaction between the $-R$ p-substituents and the first atom of the side chain is precluded in both states of this equilibrium) may be regarded as leveling effects since the acid-weakening resonance effects (R-values) are not as great as predicted by $\sigma_R^0\rho$. Sutton has discussed dipole moment evidence for the mutual reduction of the degree of charge delocalization by two *para* – R substituents.[28] Branch and Calvin have also considered this effect.[14a] It is clear from Fig. 2 that the most polarizable substituents are the ones which show the leveling effect.

It is also of interest that the p-fluoro substituent shows a somewhat greater acid-weakening resonance effect than expected. This result is very likely attributable to concerted inductive-mesomeric action,[29] in which the polarization of the σ and π Ar–F bonds by the electron-rich phenoxide ion (through the σ-bonds of the ring) actually assists delocalization of charge through the π bond:



The $\bar{\sigma}_R{}^p$-values for the p-fluoro substituent show this effect in all nucleophilic reactivities (reactions C.1, C.6, C.9, C.10, C.11, C.12, C.13 of Table II, ref. 2) with values ranging from -0.44 to -0.51 compared to the σ_R^0-value of -0.35. This concerted inductive-mesomeric action is apparently strongly dependent upon the electronegativity of the first atom of the substituent so that only for fluorine is the effect clearly seen. The counterbalancing of this effect by the leveling effect may be the reason that the p-methoxy substituent (or for that matter the other p-halogens) falls very near the line of Fig. 2.

Further results from the use of the σ_R^0-scale to estimate special resonance and polarization effects will be discussed in subsequent papers.

Experimental

Instrumentation and Measurements.—The F^{19} spectra of m- and p-substituted fluorobenzenes are complicated by the splittings induced by the o-hydrogens and as a result may not be examined by use of the highly accurate wiggle beat[30,31] method against a close lying standard resonance line. The average F^{19} substituted fluorobenzene resonance spectra is spread over about 10 c.p.s. with considerable structuring; the lack of a clearly dominant peak of the same origin for all the compounds considered is also to be noted.

Relatively rapid field sweep provides envelopes (of the above-mentioned structures) which are sufficiently narrow to be measured by means of generated side bands to ± 5 c.p.s.[32] Both the methods of matching, and measuring distances between side bands were employed. The side-bands were pro-

Table XI

Results

δ (c.p.s.) = $-400\ \delta^F$

Method A Substituent	Source[a]	Method A Neat	Method A Extrap. → 0	Method B 5%, C_6H_5F, XC_6H_5F
H	1	0	0	0
p-NO_2	1	−410	−396	−386
p-CHO	2			−375
p-CN	1	−420	−370	−374
p-$COCH_3$	2			−263
p-COOEt	2			−242
p-Br	1	47	96	101
m-Br	2			− 87
p-Cl	3			126
m-Cl	1	−114		− 78
p-F	3			271
m-F	3			−119
p-CH_3	1	214	240	215
m-CH_3	1	45		48
p-$NHCOCH_3$	2			
m-$NHCOCH_3$	2			− 42
p-OH	4			430
p-OCH_3	1	455	455	460
m-OCH_3	2			− 43
p-NH_2	4			563
m-NH_2	1			− 8
p-CF_3	2			−204
m-CF_3	3			− 85
p-C_6H_5	1			126

[a] 1, Eastman Organic Chemicals, White Label, D.P.I., Rochester, N. Y.; 2, L. Light and Co. Ltd., Poyle Colnbrook, Bucks, Eng.; 3, Dr. G. C. Finger, Illinois Geological Survey, Urbana, Ill.; 4, Aldrich Chemical Co., Inc., Milwaukee, Wis.

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(28) L. E. Sutton in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, New York, N. Y., 1955, p. 411.

(29) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

(30) A. A. Bothner-By and R. E. Glick, *ibid.*, **26**, 362 (1956).

(31) C. A. Reilly, *ibid.*, **25**, 604 (1956).

(32) J. T. Arnold and M. G. Packard, *ibid.*, **19**, 1608 (1951).

duced with a Hewlett–Packard model 202-A low-frequency function generator and the spectra obtained on a Varian Associates model V 4300B spectrometer operating at 40.01 mc. Spinning of the sample was always employed unless the signal to noise ratio obtained in the high dilution runs precluded any advantage from this homogenization procedure. Visual observation and measurement of the side bands was carried out on the oscilloscope in some cases, and in the others the Sanborn recorder was employed and the output in c.p.s. counted from the chart paper.

Sample Preparations. Method A, external standard procedure: Into 5-mm. outside diameter Pyrex tubes were sealed solutions of the substituted fluorobenzene in solvent along with sealed 1-mm. capillaries containing the standard, (a) solution prepared by adding 10 ml. of saturated KOH solution to 40 ml. of saturated KF, (*b*) neat (C_6H_5F). Concentrations of 25, 50, 75 and 100 volume per cent. solute were prepared within the sample tube by delivering appropriate amounts of the liquids from a 1-ml. syringe; the total volume being 0.4 ml., neglecting small shrinkage effects. The tubes were thoroughly mixed by shaking before examination.

Method B, internal standard (5 volume per cent.) procedure: Into 5-mm. o.d. Pyrex tubes were delivered 0.54 ml. of solvent and 0.03 ml. of both C_6H_5F and the substituted fluorobenzene, the former from a 1-ml. syringe, the latter from a 0.100-ml. syringe. The tubes were sealed and thoroughly shaken before examination. Results are listed in Table XI.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, AMERICAN VISCOSE CORPORATION]

Isomorphous Replacement in Copolyamide Systems. Homologs of Adipic and Terephthalic Acids

BY ARTHUR J. YU[1] AND ROBERT D. EVANS

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Four pairs of comonomers—(1) suberic acid/*p*-benzenediacetic acid, (2) sebacic acid/*p*-benzenedipropionic acid, (3) hexamethylenediamine/*p*-xylene-α,α'-diamine, (4) octamethylene-diamine/2,2′-*p*-phenylene-bis-ethylamine—were used to prepare a series of copolyamides. Comonomer pairs 1 and 2 can be considered as homologs of adipic and terephthalic acids; comonomer pairs 3 and 4 are the amino analogs of 1 and 2. The members of each pair bear the same structural relationship as adipic and terephthalic acids. It was found that copolyamides containing comonomer pairs 2 and 4, in which the number of methylene groups between the benzene ring and the functional groups is even, were isomorphous, whereas copolyamides containing comonomer pairs 1 and 3, in which the number of methylene group is odd, were not isomorphous. A lattice model for crystallization of copolyamides was proposed to correlate the experimental results.

Introduction

Isomorphous replacement of adipic and terephthalic acids in copolyamide systems was first suggested by Edgar and Hill.[2] Our work, reported elsewhere,[3] has substantiated this finding, and also established the effect of diamine structure on the isomorphism of these two diacids. In general, adipic and terephthalic acids will form isomorphous copolyamide systems with straight chain aliphatic diamines. The melting point *vs.* composition curves of these systems are sigmoidal and have no minimum at the intermediate ranges of composition. Since the structural difference of adipic and terephthalic acids involves the separation of carboxyl groups in the former by four methylene groups, and in the latter by a *p*-phenylene unit, it is the purpose of this work to investigate whether other comonomer pairs, with the same structural difference as adipic and terephthalic acids, can also be isomorphous in copolyamide systems. Four pairs of comonomers were selected: (1) suberic acid and, *p*-benzenediacetic acid, (2) sebacic acid and *p*-benzenedipropionic acid, (3) hexamethylenediamine and *p*-xylene-α,α'-diamine, and (4) octamethylenediamine and 2,2′-bis-phenylene-bis-ethylamine.

Comonomer pairs 1 and 2 can be considered as homologs of adipic and terephthalic acids. Comonomer pairs 3 and 4 are the amino analogs of 1 and 2. Copolyamides were prepared from these comonomer pairs with aliphatic straight chain diamines or diacids, and a melting point *vs.* composition curve was plotted for each system. The presence or absence of minima in these curves will indicate the isomorphous replacement of four methylene groups by a *p*-phenylene unit in the copolyamide systems under study. This information could lead to the understanding of the mechanism of polymer isomorphism.

Experimental

Chemicals.—Adipic acid, suberic acid, azelaic acid, sebacic acid, hexamethylenediamine and octamethylenediamine were purchased.

p-Benzenediacetic acid, m.p. 250–252°, was prepared by the method of Kipping,[4] except α,α'-dichloro-*p*-xylene was used instead of the corresponding dibromo compound.

p-Benzenedipropionic acid, m.p. 232°, was prepared by the catalytic hydrogenation of *p*-benzenediacrylic acid[5] in sodium hydroxide solution.

p-Xylene-α,α'-diamine was prepared from α,α'-dichloro-*p*-xylene and hexamethylenetetramine. A mixture of 280 g. (2 moles) of hexamethylenetetramine, 176 g. (1 mole) of α,α'-dichloro-*p*-xylene and 3.5 l. of chloroform was refluxed for 3 hr. to give 403 g. (89%) of the di-quaternary hexaminium salt. The quaternary salt was warmed at 50° with stirring in 3 l. of absolute ethanol containing about 300 g. of anhyd. hydrogen chloride. After the diamine di-hydrochloride precipitated, the mixture was refluxed for 3 hr. The diamine di-hydrochloride was then collected, dried, and dissolved portionwise in excess sodium hydroxide solution. The organic layer was extracted with benzene. Removal of benzene gave 115 g. (95% based on the quaternary hexaminium salt) of crude *p*-xylene-α,α'-diamine. Distillation under reduced pressure gave the purified product, b.p. 120–123° (0.5 mm.), m.p. 44–46°. *Anal.* Calcd. for $C_8H_{12}N_2$: C,

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(1) Thiokol Chemical Corporation, Trenton, N. J.

(2) O. B. Edgar and R. Hill, *J. Polymer Sci.*, **8**, 1 (1952).

(3) A. J. Yu and R. D. Evans, presented at the 135th American Chemical Society Meeting, Boston, Mass., 1959.

(4) J. S. Kipping, *Ber.*, **21**, 42 (1888).

(5) P. Ruggli and W. Theilheimer, *Helv. Chim. Acta*, **24**, 899 (1941).