Substituent Effects. IV.[1-3] A Reexamination of σ^n, $\Delta\sigma_R^+$, and σ_R^n Values; Arylacetic Acids, and Other Insulated Systems

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Abstract: Thermodynamic dissociation constants have been determined for phenylacetic acid and 36 derivatives in 10, 50, and 75% ethanol–water mixtures. The derived σ values and those from other "insulated" reaction series are given and their averages are tabulated. The σ^n values for 4-NH_2 and 4-NMe_2 differ considerably from those listed by Taft and by Yukawa and Tsuno; a criticism is presented. New $\Delta\sigma_R^+$ values are derived and tabulated, and some remarks on the Yukawa–Tsuno equations are made. New values for σ_R^n (σ_R^0) show a remarkable constancy for simple first-row substituents. Arylacetic acids, and possibly other "insulated" reaction systems as well, are unsatisfactory for deriving σ^n values of $-M$ substituents; the values of σ obtained are somewhat exalted.

It is generally recognized[1-8a] that the Hammett equation[8b]

$$\log K - \log K^0 = \rho\sigma \qquad (1)$$

fails with a $-M$ substituent in para position to a $+M$ reaction center, as also with a $+M$ substituent para to a $-M$ reaction center. The classical example is the acid–base equilibrium of 4-nitroanilinium ion in which the exaltation of σ observed for the nitro group is ascribed to the through-resonance interaction in 4-nitroaniline. Similarly, in the carboxylic acid–base equilibrium of 4-aminobenzoic acid, the $+M$ amino substituent interacts (differently) with the $-M$ reaction centers COOH and COO^-, causing the σ value of the amino group to be exalted. In other reaction series the exaltations of one and the same substituent are larger or smaller and, consequently, a multiplicity of σ values is observed.

On the other hand, the combination $-M$ substituent *vs.* $-M$ reaction center, as well as the combination $+M$ substituent *vs.* $+M$ reaction center, are considered to show unexalted, normal σ values for para substituents. This implies that the defining reaction series, the dissociation constants of benzoic acids in water at 25°, with $\rho \equiv 1$, gives normal σ_p values for $-M$ substituents but, as indicated, gives exalted σ_p values for $+M$ substituents.

The derivation of normal σ_p values (σ_p^n) for $+M$ substituents was obviously desirable both for predictive purposes and for theoretical work. Two approaches were suggested by Jaffé:[11] "The "normal" substituent constants for the electron-releasing substituents (e.g., OH and NH_2) should probably be evaluated from reaction series in which either [a] the reaction site is insulated from the benzene ring (e.g., by a methylene group) or [b] the side chain itself is electron-repelling, so that [through-resonance] is unimportant."

These ideas were applied systematically by van Bekkum, *et al.*[3] These authors calculated regression lines from data believed to be unaffected by through-resonance and found that the derived normal σ values, denoted as σ^n, had relatively narrow ranges and were reasonably constant. We note here that, although both approaches were adopted in principle, more than 90% of the σ^n values thus obtained derived from $+M,+M$ combinations (and $-M,-M$ combinations), only a few suitable insulated reaction types being available at the time.

Taft, *et al.*,[5] derived normal σ values, denoted as σ^0, by the first approach, *i.e.*, by concentrating on systems insulated by a methylene group. This, and similar work by other groups, is a subject of discussion in the present paper.

A third approach to σ^n values uses steric hindrance to planarity as a means to achieve or approach conjugative insulation. It is severely restricted since the conjugation of reaction centers like NH_2 and OH with an aromatic ring is almost immune to this type of steric hindrance, but the method has provided some additional independent data.[12]

These three approaches, each with its own specific strong and weak points, give σ^n values which are mostly

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[1] Part III: A. J. Hoefnagel, J. C. Monshouwer, E. C. G. Snorn, and B. M. Wepster, *J. Amer. Chem. Soc.*, **95**, 5350 (1973).

[2] Part II: B. M. Wepster, *ibid.*, **95**, 102 (1973).

[3] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 78, 815 (1959).

[4] H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953).

[5] (a) R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, 81, 5343 (1959); (b) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, 81, 5352 (1959); (c) R. W. Taft, Jr., *J. Phys. Chem.*, 64, 1805 (1960).

[6] (a) Y. Tsuno, T. Ibata, and Y. Yukawa, *Bull. Chem. Soc. Jap.*, 32, 960 (1959); (b) Y. Yukawa and Y. Tsuno, *ibid.*, 32, 965 (1959); (c) *ibid.*, 32, 971 (1959); (d) Y. Yukawa, Y. Tsuno, and M. Sawada, *ibid.*, **39**, 2274 (1966); (e) *ibid.*, **45**, 1198 (1972).

[7] Y. Yukawa, *Yuki Gosei Kagaku Kyokai Shi*, special ed, 69 (1962); M. Yoshioka, K. Hamamoto, and T. Kubota, *Bull. Chem. Soc. Jap.*, 35, 1723 (1962).

[8] (a) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970. (b) Most of the definitions and notations have been explained in the accompanying part III.[1] For σ, $\bar{\sigma}$, and $\bar{\bar{\sigma}}$ see footnote 9. Other symbols and equations are introduced in the text; some of our reasons to retain the notation σ^n are given in footnote 3 of part II.[2]

[9] Yukawa, *et al.*, apparently define log K^0 in $(\log K - \log K^0)/\rho$ from the intercept of the regression line; we use the notation $\bar{\bar{\sigma}}$ for the σ values thus defined. Taft[5] originally defined $\bar{\sigma} = (\Delta \log K)/\rho$ and intends to use the experimental value of the unsubstituted compound (private communication). Our σ values are calculated as discussed by Jaffé.[4] We note that the differences between the σ values from methods 4 and 5 of Table V are much less for $\bar{\bar{\sigma}}$ than for σ and $\bar{\sigma}$. Again, the standard deviations of $\bar{\bar{\sigma}}$ (Tables X and XI[10]) are considerably smaller than those of σ and $\bar{\sigma}$.

[10] These data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-5357. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

[11] Reference 4, p 230.

[12] Unpublished work from this laboratory; *cf.* ref 3, p 833, footnote 16, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 75, 1473 (1956).

Table I. Thermodynamic pK_a* Values[a] of $ArCH_2COOH$ in Various Ethanol–Water Mixtures at 25°

	Solvent[d]				Solvent[d]		
Substituents	10%	50%	75%	Substituents	10%	50%	75%
3,5-Di-Me	4.61	5.63	6.32	4-Me	4.57	5.56	6.32
3-Me	4.56	5.56	6.27	*i*-Pr		5.60	6.32
H[e]	4.50	5.47	6.20	*t*-Bu		5.60	6.32
3-F	4.34	5.29	5.96	*neo*-Pent		5.61	6.31
Cl	4.33	5.28	5.92	$CH_2NH_3^+Cl^-$ [e]	4.03	4.77	5.29
Br	4.33	5.28	5.92	CN	4.11	4.95	5.58
I		5.31	5.96	NH_2		(5.61)[b]	6.39[c]
NO_2[e]	4.14	4.98	5.61	NMe_2		(5.63)[b]	6.39
				NHFo	4.42	5.36	6.12
3-*t*-Bu		5.65	6.34	NHAc	4.44	5.43	6.18
3,5-Di-*t*-Bu		5.79	6.46	$NMe_3^+I^-$ [e]	3.89	4.51	5.05
3-$CH_2NH_3^+Cl^-$ [e]	3.99	4.65	5.09	NO_2[e]	4.05	4.86	5.51
CN	4.18	5.02	5.67	OH	4.59	5.59	6.39
NH_2			(6.27)[c]	OMe	4.55	5.53	6.30
$NMe_3^+I^-$ [e]	3.80	4.32	4.75	OPh	4.50	5.44	6.16
OH	4.49	5.45	6.21	F	4.43	5.36	6.06
OMe	4.49	5.43	6.19	Cl	4.37	5.28	5.95
				Br	4.36	5.28	5.96
3-*t*-Bu-4-NO_2		5.15		I	4.36	5.25	5.95
3,5-Di-Me-4-NO_2		5.13	5.78				

[a] If, with the amino acids, the sum of the corrections for zwitterion and ammoniocarboxylic acid is larger than 0.02 unit, the corrected pK_a* value is bracketed; for details see footnotes *b* and *c*. Where parentheses and superscripts are absent, the correction is negligible. The ammonio acids need no correction. [b] "Overall" value in 50% ethanol: 4-NH_2, 5.72; 4-NMe_2, 5.79. [c] "Overall" value in 75% ethanol: 3-NH_2, 6.32; 4-NH_2, 6.41. [d] 10, 50, and 75%: 10, 50, and 75 volumes of absolute ethanol in 100 volumes of final solution; *cf.* Experimental Section. [e] In water: H, 4.31 (ref 38, 4.312); 3-NO_2, 3.97 (ref 38, 3.967); 4-NO_2 was extrapolated from values in 10, 4, and 2 vol % ethanol; 3.89 (ref 38, 3.851; *cf.* ref 37); 3-$CH_2NH_3^+$, 3.83; 3-NMe_3^+, 3.66; 4-$CH_2NH_3^+$, 3.88; 4-NMe_3^+, 3.75.

in good agreement with one another. This allows the conclusion that the use of σ^n for the quantitative separation of "normal" and through-resonance effects has a firm empirical background. However, the soundness of this conclusion is marred to some extent by the fact that the evidence for certain important substituents is sketchy and partially conflicting. As part of an investigation to assess whether these discrepancies are real or apparent, we have measured the dissociation constants of a series of arylacetic acids in various solvents. The data are reported here and are discussed, together with those described in the accompanying paper[1] on β-arylpropionic acids and β-arylisovaleric acids and with the available literature data on these and related reaction series.

The σ values found for the positive poles will be discussed in a separate paper in relation to those for the benzoic acid series, as will be the observed meta σ^n values (σ_m^n or σ_m).

Results

Table I lists the thermodynamic dissociation constants of the arylacetic acids obtained in this study. Table II gives the reaction constants ρ (ρ_m) and other statistical data, using, as previously,[1] the standard σ values of: (1) 3,5-di-Me; (2) 3-Me; (3) H; (4) 3-F; (5) 3-Cl; (6) 3-Br; (7) 3-I; (8) 3-COMe; (9) 3-NO_2; and (10) 3,5-di-NO_2.

Table II also gives the same information for some other reaction series from the literature. The data pertaining to the reaction series 11, 12, and 13 do not, in our opinion, belong to the same type but have been included since these data have been used by Taft, *et al.*,[5b,c] in their derivation of σ^0 values (see Discussion).

Table III gives the individual σ values, calculated as before.[1,3] Table IV summarizes average σ and $\bar{\sigma}$ values for +M and ±M substituents, and, for comparison, the values listed as σ^n in part I of this series,[3] and as σ^0 by Taft and by Yukawa, *et al.*;[6d,e] values of $\Delta\sigma_R^+$ and σ^+ are included. Table VI summarizes the data for −M substituents and includes $\Delta\sigma_R^-$ and σ^- values. Preferred values are in boldfaced type.

Discussion

As shown in Table II all correlations obtained for meta-substituted insulated systems are satisfactory. Perhaps some are not as good as might have been hoped for (see, *e.g.*, reactions 1d and 10), but we have no convincing reasons to omit any of them.

The individual σ values calculated for each of the +M and −M substituents exhibit a considerable variation, as shown in Table III. This is not unusual, as follows from data in part I,[3] but it has been very often masked by judging the constancy of σ only from the statistical data of regression lines obtained using meta and para data.[6d] Part of this variation, as is also part of the differences between σ and $\bar{\sigma}$, undoubtedly is due to experimental error, the effect of which on σ values is aggrevated the lower the ρ values; part of it is believed to be real, as, for instance, the variations observed with the positive poles, 4-*t*-Bu[13] and 3,5-di-*t*-Bu[13] and 4-OH and 4-NHAc. Table III demonstrates the changes in going from one reaction series to another, from one solvent to another, and from one group of workers to another. It is, of course, not feasible to discuss all possible intercomparisons, but a few generalizations are now offered.

+M Substituents. Inspection of the σ values for reactions 1–10 in Table III, although revealing some exceptional σ values, provides little indication that any of these reaction series deviates strongly from any of the others. Accordingly, we feel justified in discussing the average values as σ^n values (Table IV).

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(13) *Cf.* J. M. Wilson, A. G. Briggs, J. E. Sawbridge, P. Tickle, and J. J. Zuckerman, *J. Chem. Soc. A*, 1024 (1970).

Table II. Reaction Constants and Other Statistical Data[a]

No.	Reaction	Solvent	Temp, °C	$\rho \pm s_\rho$	s	R	Δ^0	Substituents
1a	$ArCH_2COOH$	H_2O[b]	25	0.486 ± 0.022	0.011	0.998	−0.007	3, 5, 7, 9
b		H_2O[c]	25	0.504 ± 0.018	0.009	0.999	0.006	3, 4, 5, 9
c		10% EtOH	25	0.543 ± 0.027	0.020	0.994	−0.029	1, 2, 3, 4, 5, 6, 9
d		50% EtOH	25	0.714 ± 0.052	0.038	0.985	−0.058	1, 2, 3, 4, 5, 6, 7, 9
e		75% EtOH	25	0.828 ± 0.030	0.022	0.996	−0.027	1, 2, 3, 4, 5, 6, 7, 9
2a	$ArCH_2COOH + Ph_2CN_2$	EtOH[d]	36	0.412[d]				
b		EtOH[e]	30	0.400 ± 0.016	0.010	0.998	0.011	2, 3, 5, 9
c		2-Methylbutanol-1[e]	30	0.741 ± 0.021	0.013	0.999	0.004	2, 3, 5, 9
3a	$ArCH_2COOEt + OH^-$	85% EtOH[f]	25	1.245 ± 0.038	0.019	0.999	−0.013	3, 5, 7, 9
b		88% EtOH[g]	30	1.192[g]				
c		56% acetone[h]	25	0.903 ± 0.048	0.030	0.996	−0.008	2, 3, 4, 5, 9
d		56% acetone[i]	25	0.975 ± 0.037	0.024	0.996	−0.005	2, 3, 4, 5, 6, 8, 9
4a	$ArCH_2CH_2COOH$	10% EtOH[j]	25	0.268 ± 0.009	0.009	0.999	−0.003	3, 9, 10
b		50% EtOH[j]	25	0.385 ± 0.019	0.025	0.994	−0.033	1, 2, 3, 5, 6, 9, 10
c		75% EtOH[j]	25	0.448 ± 0.007	0.009	0.999	−0.006	1, 2, 3, 5, 6, 9, 10
5	$ArCH_2CH_2COOEt + OH^-$	88% EtOH[k]	30	0.635 ± 0.016	0.010	0.999	0.004	2, 3, 5, 9
6a	$ArCMe_2CH_2COOH$	50% EtOH[j]	25	0.377 ± 0.043	0.021	0.988	−0.014	3, 5, 6, 9
b		75% EtOH[j]	25	0.448 ± 0.047	0.024	0.989	−0.015	3, 5, 6, 9
7	$ArCH_2NH_3^+$	H_2O[l]	25	1.023 ± 0.009	0.006	1.000	−0.002	2, 3, 4, 5, 6, 9
8	$ArCH_2N^+H_2$-2,4-di-NO_2Ph	H_2O[m]	25	1.702 ± 0.078	0.049	0.997	−0.050	2, 3, 4, 6, 9
9	$ArCH_2NH_2$ + 1-Cl-2,4-di-NO_2-Ph	96% EtOH[n]	45	−0.777 ± 0.037	0.024	0.996	0.008	2, 3, 4, 5, 6, 9
10	$ArCH_2OAc + OH^-$	56% acetone[o]	25	0.712 ± 0.082	0.051	0.987	−0.043	2, 3, 7, 9
11	ArCOOH	Benzene[p]	25	−2.161 ± 0.023	0.030	1.000	−0.006	1, 2, 3, 4, 5, 6, 7, 9, 10
12	ArCOOH, ir ν_{OH}	CCl_4[q]	25	11.258 ± 0.333	0.167	1.000	−0.064	3, 5, 9
13a	$ArPO_3H^-$	H_2O[r]	25	1.121 ± 0.074	0.037	0.996	−0.013	3, 5, 6, 9
b		50% EtOH[r]	25	1.153 ± 0.196	0.099	0.972	−0.062	3, 5, 6, 9

[a] ρ, reaction constant; s_ρ, standard deviation of ρ; s, standard deviation of the experimental points; R, correlation coefficient; Δ^0, intercept regression line with ordinate ($\sigma = 0$) − log K_a* observed for unsubstituted compound; substituents, actual substituents in the compounds involved in the calculation of ρ, identified according to their number mentioned in the text. [b] Reference 38. [c] A. Fischer, B. R. Mann, and J. Vaughan, *J. Chem. Soc.*, 1093 (1961). [d] R. M. O'Ferrall and S. I. Miller, *J. Amer. Chem. Soc.*, **85**, 2440 (1963). The data at 26° for the substituents 3, 5, 6, 7, and 9 give a regression line with $\rho = 0.411$, $s = 0.021$, $R = 0.985$, and $\Delta^0 = 0.01$; the correlation of *all* data available at both 26 and 36° ($n = 8$) gives a regression line with slope 1.001, $R = 0.996$, $\Delta^0 = -0.01$; the product of this slope and ρ at 26° was taken as ρ at 36°; $\bar{\sigma}$ values follow. [e] N. B. Chapman, J. R. Lee, and J. Shorter, *J. Chem. Soc. B*, 769 (1969); the two solvents, chosen out of six, are those giving the highest and the lowest value of σ-4-NO_2. [f] J. G. Watkinson, W. Watson, and B. L. Yates, *ibid.*, 5437 (1963). [g] K. Kindler, *Justus Liebigs Ann. Chem.*, **452**, 90 (1927). The correlation of the data for *all* compounds common to reactions 3a and 3b ($n = 6$) gives a regression line with slope 0.958, $R = 0.999$, $\Delta^0 = 0.02$; the product of this slope and ρ of reaction 3a was taken as ρ of reaction 3b; $\bar{\sigma}$ values follow. [h] R. O. C. Norman, G. K. Radda, D. A. Brimacombe, P. D. Ralph, and E. M. Smith, *J. Chem. Soc.*, 3247 (1961); R. O. C. Norman and P. D. Ralph, *ibid.*, 5431 (1963). [i] Reference 6d. [j] Reference 1. [k] R. Fuchs and J. A. Caputo, *J. Org. Chem.*, **31**, 1524 (1966). [l] L. F. Blackwell, A. Fischer, I. J. Miller, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 3588 (1964). [m] A. Fischer, M. P. Hartshorn, U. M. Senanayake, and J. Vaughan, *J. Chem. Soc. B*, 833 (1967). [n] A. Fischer, R. S. H. Hickford, G. R. Scott, and J. Vaughan, *ibid.*, 466 (1966). [o] E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938); E. Tommila, *Ann. Acad. Sci. Fenn. Ser. A*, **59**, No. 4 (1942). [p] M. M. Davis and H. B. Hetzer, *J. Res. Nat. Bur. Stand.*, **60**, 569 (1958). [q] J. D. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954). [r] H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Amer. Chem. Soc.*, **75**, 2209 (1953).

The average σ^n values of reactions 1–10 are found to be in satisfactory agreement with the average σ^n values obtained in part I,[3] taking into account the uncertainties of the experimental data and the inherent limitations of the Hammett equation. This agreement strengthens the view that σ^n values from insulated systems and noninsulated systems are equivalent, and that, therefore, the σ^n concept is basically correct and useful; at the same time it provides further justification for the quantitative separation of normal and through-resonance effects.

The agreement between the σ^n values and the σ^0 values of Taft and of Yukawa, *et al.*, is mostly good. There are, however, two important exceptions. The σ^0 values listed for 4-NH_2 and 4-NMe_2 are 0.12–0.24 unit more negative than our present σ^n values; in fact, they are more negative than any one value observed with reactions 1–10. Obviously, some comment is needed.

Taft's σ^0 Values. In 1959, in their derivation of σ^0 values (*via* $\sigma_R{}^0$ values), Taft, *et al.*,[5b] adopted three insulated reaction series of the type $ArCH_2Y$ as a basis: (B.1) pK_a $ArCH_2COOH$ (our reaction no. 1a); (B.2) saponification $ArCH_2COOEt$ 88% aq C_2H_5OH (our no. 3b); and (B.14) saponification $ArCH_2OCOCH_3$ 60% aq acetone (our no. 10). In a following paper[5c] a fourth reaction series was mentioned [(B.3) pK_a $ArCH_2CH_2COOH$ (*cf.* our no. 4)] but it was probably used only indirectly.[14]

In the latter paper, which as a rule is quoted as the source of Taft's σ^0 values, it is stated that the listed values all derive from the data on the $ArCH_2Y$ systems mentioned. However, when turning to the earlier paper[5b] or the original literature, it appears that for these reactions there was no datum available at the time for 4-NMe_2 (nor for 4-NHAc, OH, SMe, or Ph) and only one for 4-NH_2. As to the value given for 4-NMe_2, this has been derived from infrared data on benzoic acids in CCl_4 (ν_{OH}; our no. 12) which are not accurate, which should give exalted values, and which, according to our calculations, give σ-4-NMe_2 = −0.79. As to the value given for 4-NH_2, this stems from reaction B.2. However, for this reaction the lack of suitable data prevented the usual calculation, and σ values were obtained[14] by: (a) taking ρ (ρ_I) as 1/2.5 of the ρ value for the alkaline hydrolysis of

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(14) Reference 5a, Table II, footnote *e*.

Table III. Calculated σ Values[a]

No.	σ
4-Me	
1a	−0.103
b	−0.110
c	−0.072
d	−0.036
e	−0.110
2b	−0.114
c	−0.094
3a	−0.061
b	−0.030[b]
c	−0.144
d	−0.116
5	−0.128
6a	−0.084
7	−0.154
8	−0.086
9	−0.106
10	−0.144
11	−0.103
13a	−0.136
b	−0.027
4-Et	
1a	−0.109
3d	−0.122
4-*i*-Pr	
1a	−0.148
d	−0.090
e	−0.110
3a	−0.035[c]
c	−0.150[c]
d	−0.147[d]
10	−0.330
3-*t*-Bu	
1d	−0.158
e	−0.134
4-*t*-Bu	
1a	−0.201
d	−0.090
e	−0.110
3a	−0.033
c	−0.322
d	−0.164
6a	−0.084
4-*neo*-Pent	
1d	−0.104
e	−0.098
3a	−0.044[c]
c	−0.167[c]
4-Ph	
3c	0.067
d	0.048
3,4-Benzo	
3c	0.061
d	0.070
3-$CH_2NH_3^+$	
1a	1.000
c	0.983
d	1.201
e	1.364
4a	1.839
4b	1.810
c	2.198
4-$CH_2NH_3^+$	
1a	0.898
c	0.911
d	1.038
e	1.124
4a	1.615
b	1.450
c	1.686
4-COMe	
3c	0.528
d	0.497
3-CN	
1c	0.638
d	0.698
e	0.669
4b	0.681
c	0.705
8	0.650
9	0.610
11	0.604
4-CN	
1c	0.765
d	0.793
e	0.777
3c	0.772
4b	0.758
c	0.817
6a	0.847
b	0.784
7	0.842
8	0.732
9	0.655
10	0.684
11	0.590
3-COO^-	
13a	0.050
b	0.145
4-COO^-	
13a	0.174
b	0.162
4-NO_2	
1a	0.961[e]
c	0.874
d	0.915
e	0.861
2a	0.668[b]
b	0.691
c	0.770
3a	0.725
b	0.718[b]
c	0.862
d	0.814
4b	0.886
c	0.928
5	0.793
6a	0.976
b	0.871
7	0.862
8	0.808
9	0.704
10	0.868
11	0.715
12	0.805
13a	0.758
b	0.760
3-NH_2	
1e	(−0.050)
4c	−0.142
5	−0.212
11	−0.150
13a	−0.065
b	+0.030
4-NH_2	
1d	(−0.104)
e	−0.194
2a	−0.277[b]
3a	−0.231
b	−0.245[b]
c	−0.154
4b	(−0.166)
c	−0.260
5	−0.333
6a	(−0.136)
b	−0.222
11	−0.372
12	−0.615
13a	−0.392
3-NHMe	
13a	−0.189
4-NHMe	
13a	−0.436
3-NHEt	
13a	−0.136
3-NHnBu	
13a	−0.215
3-NMe_2	
5	−0.157
11	−0.168
4-NMe_2	
1d	(−0.131)
e	−0.194
3c	−0.243
5	−0.271
12	−0.793
4-$NHNH_2$	
13a	−0.401
4-NHFo	
1c	0.201
d	0.236
e	0.130
4-NHAc	
1c	0.165
d	0.141
e	0.058
6a	0.200
13a	−0.012
b	0.104
3-NMe_3^+	
1a	1.349
c	1.329
d	1.649
e	1.771
3c	1.455
4a	2.025
b	2.272
c	2.555
5	1.156
4-NMe_3^+	
1a	1.164
c	1.165
d	1.391
e	1.412
3a	0.715
c	1.186
4a	1.801
b	1.810
c	2.087
5	0.844
6a	2.036
b	2.205
3-OH	
1c	0.074
d	0.114
e	0.022
11	0.045
12	0.095
13a	0.050
b	0.096
4-OH	
1c	−0.108
d	−0.077
e	−0.194
6a	−0.084
11	−0.145
12	−0.349
13a	−0.144
b	−0.117
3-OMe	
1c	0.074
d	0.141
e	0.046
2a	0.062[b]
3a	0.050
c	0.036
5	0.048
7	0.090
8	0.130
9	0.059
11	0.059
4-OMe	
1a	−0.084
b	−0.100
c	−0.035
d	0.005
e	−0.086
2a	−0.116[b]
3a	−0.033
b	−0.034[b]
c	−0.043
d	−0.090
5	−0.129
6a	−0.006
7	−0.125
8	−0.197
9	−0.154
10	−0.132
11	−0.154
12	−0.438
4-OEt	
5	−0.144
13a	−0.171
b	−0.109
4-OPh	
1c	0.056
d	0.127
e	0.082
3d	0.082
4-SMe	
3d	0.091
4-SEt	
13b	0.022
4-SO_2NH_2	
13a	0.625
b	0.678

Table III (*Continued*)

No.	σ	No.	σ	No.	σ	No.	σ
4-F		2b	0.212	3d	0.313	3a	−0.138[c]
1a	0.152	c	0.294	7	0.246	c	−0.525[c]
b	0.173	3a	0.318	8	0.253	4b	−0.372
c	0.183	b	0.340[b]	9	0.280	c	−0.164
d	0.236	c	0.389	10	0.300		
e	0.202	d	0.288	11	0.281		
2b	0.083	5	0.291	13a	0.227	3,4-CH_2O_2	
c	0.184	6a	0.304	b	0.276	5	−0.008
3a	0.225	7	0.237			13a	−0.056
c	0.230	8	0.259	4-I		b	0.014
d	0.221	9	0.310	1a	0.290		
5	0.197	10	0.320	c	0.310		
6a	0.226	11	0.262	d	0.385	3,4-Di-Cl	
7	0.080	12	0.095	e	0.333	5	0.587
8	0.084	13a	0.298	2a	0.287[b]	11	0.567
9	0.160	b	0.293	b	0.300		
10	0.219			c	0.335		
11	0.165	4-Br		3a	0.333	3-*t*-Bu-4-NO_2	
		1a	0.270	c	0.225	1d	0.521
4-Cl		c	0.310	10	0.303		
1a	0.265	d	0.345	11	0.276		
b	0.254	e	0.321			3,5-Di-Me-4-NO_2	
c	0.292	2b	0.249			1d	0.548
d	0.345	c	0.312	3,5-Di-*t*-Bu		e	0.537
e	0.333	3a	0.343	1d	−0.348	4b	0.501
2a	0.242[b]	c	0.408	e	−0.278	c	0.616

[a] Values in parentheses are considered to be less reliable due to uncertainties in the corresponding pK_a^* values; *cf.* Table I. [b] $\bar{\sigma}$ values; see footnotes *d* and *g* of Table II. [c] From unpublished data by R. O. C. Norman and D. J. Byron. Observed values for 10^3k; reaction **3a**: 4-*i*-Pr, 8.06; 4-*neo*-Pent, 7.86; 3,5-di-*t*-Bu, 6.00; reaction 3c: 4-*i*-Pr, 31.4; 4-*neo*-Pent, 30.3; 3,5-di-*t*-Bu, 14.3. [d] σ-4-*i*-Pr from 10^2k = 3.08 (Table IV, footnote *g*). [e] Using our pK_a value σ-4-NO_2 = 0.843 (see footnote 37).

Table IV. +M and ±M Substituents; Summary of Para σ Values:[p] σ^n, σ^0, $\Delta\sigma_R^+$, σ^+

	σ^n							$\Delta\sigma_R^+$		σ^+, this paper
	This paper[a]			Part I[b]		Taft,[c]	Yukawa, *et al.*,[d]	This paper[e]	Yukawa, *et al.*[f]	
Substituent	σ	*n*	$\bar{\sigma}$	σ	*n*	σ^0	σ^0			
Me	**−0.10** ± 0.04	17	−0.12	−0.13	27	−0.15	−0.12	**−0.22**	−0.19	−0.32
Et	**−0.12** ± 0.01	2	−0.13	−0.11[i]	1		−0.12	**−0.19**	−0.16	−0.31
i-Pr[g]	**−0.14** ± 0.09	7	−0.18	−0.15[i]	1		−0.15[g]	**−0.15**	−0.12	−0.29
t-Bu	**−0.14** ± 0.10	7	−0.18	−0.16[i]	2		−0.16	**−0.12**	−0.09	−0.27
neo-Pent	**−0.10** ± 0.05	4	−0.14							
Ph	**0.06** ± 0.01	2	0.05			0.00	0.05	**−0.26**[l]	−0.22	−0.21
3,4-Benzo	**0.07** ± 0.01	2	0.06				0.07		−0.20	
NH_2	**−0.24** ± 0.05	8	−0.25	−0.30	4	−0.38	−0.36[k]	**−1.23**[m]	−1.00	−1.47
NMe_2	**−0.24** ± 0.04	3	−0.25	−0.22	4	−0.44	−0.48[k]	**−1.43**[m]	−1.30	−1.67
NHFo	**0.19** ± 0.05	3	0.13							
NHAc	**0.14** ± 0.06	4	0.09			0.03		**−0.72**		−0.58
OH	**−0.12** ± 0.05	4	−0.17	−0.20	7	−0.13	−0.16[k]	**−0.79**	−0.82	−0.91
OMe	**−0.09** ± 0.06	16	−0.11	−0.18	20	−0.12 −0.16	−0.09	**−0.71**	−0.68	−0.79
OEt	**−0.14**	1	−0.14	−0.28	2					
OPh	**0.09** ± 0.03	4	0.04				0.08	**−0.68**[n]		
O^-	**−0.50**[h]							**−1.8**[o]		−2.3
SMe	**0.09**	1	0.08				0.09	**−0.71**	−0.68	−0.62
F	**0.18** ± 0.05	16	0.16	0.06[j]	5	0.17	0.22	**−0.26**	−0.29	−0.08
Cl	**0.29** ± 0.04	18	0.28	0.24	30	0.27	0.29	**−0.19**	−0.17	0.11
Br	**0.30** ± 0.05	13	0.28	0.27	18	0.26	0.31	**−0.16**	−0.15	0.14
I	**0.31** ± 0.04	10	0.29	0.30	8	0.27		**−0.18**		0.13

[a] σ, average σ^n value for reactions 1–10, with its standard deviation; *n*, number of data; $\bar{\sigma}$, average of $\bar{\sigma}^n$ values. [b] Reference 3. [c] Reference 5c, and, for some cases, 5b; the footnotes to the tables of σ^0 in these papers, referring to solvent dependence, have not been obtained from data on $ArCH_2Y$ systems. [d] Recalculated; the differences with the figures given in ref 6d are minor. [e] Derived as explained in text. [f] Reference 6d. [g] Reference 6d gives for 4-*i*-Pr 10^2k = 3.80. This should read 10^2k = 3.08 (private communication by Y. Tsuno). [h] From data by E. Tommila, A. Nurro, R. Murén, S. Merenheimo, and E. Vuorinen, *Suom. Kemistilehti*, *B*, **32**, 115 (1959), we calculate σ of 4-O^- = −0.99 for the alkaline hydrolysis of ethyl benzoates in 56% acetone, at 25° ($\rho = 2.484$, $s = 0.078$, $R = 0.998$; substituents 2, 3, 5, and 4-NO_2). Equation 3 of ref 3 then gives the change in through-resonance interaction as $-\Delta\Delta G_p = 2.484(-0.99 - \sigma^n)1.364$. Again, according to ref 2, the through-resonance energy in para $^-OC_6H_4COOMe$ can be calculated; using $\Delta\sigma_R^+$-O^- = −1.8 (ref 2) and $\Delta\sigma_R^-$-COOMe = 0.28, $-\Delta G_p$ = 1.65 kcal/mol. Equating this ΔG to $\Delta\Delta G_p$, *i.e.*, assuming through-resonance to be absent in the transition state of the ester hydrolysis (*cf.* ref 3 and this paper), σ^n for O^- follows. Similar values are obtained by calculating r^+ of the ester hydrolysis from eq 11 of ref 2, or from the observed σ-4-NH_2 = −0.59. [i] Reaction 8 of ref 3 was recalculated omitting 4-NO_2 (reaction 1a). [j] See Discussion, ref 3. [k] Reference 6d: "Derived from other reactivities statistically"; see text. [l] From data of ref 6a, and scaling through 4-OMe only (*cf.* text). [m] In ref 1, $\Delta\sigma_R^+$-NHMe was taken as the average of the values for NH_2 and NMe_2. [n] From data by J. Miller, *Aust. J. Chem.*, **9**, 61 (1956), on halogenation of substituted benzenes, and scaling through 4-OMe only (*cf.* text). [o] Reference 2. [p] Preferred values are in boldfaced type.

ethyl benzoates in the same solvent (giving $\rho = 1.00$; our value 1.19), and (b) adjusting[15] all log k/k^0 by -0.09. The value thus derived was in fair agreement with those obtained from the data on the reactions 11–13a of our Table II, as were the values for some other substituents, and this was considered as evidence that these reactions are of the σ^0 type. We find for σ-4-NH_2 in these reactions -0.37, -0.62, and -0.39, respectively, and, on structural and other grounds, believe them to be exalted; the same view has been expressed recently by Taft, *et al.*,[16] with respect to reaction 11. Our conclusion is that the values given by Taft, *et al.*,[5b,c] for 4-NMe_2 and 4-NH_2 (and several other substituents) are not σ^n values, and therefore do not provide evidence against the values obtained in the present paper.

We note that the above criticism against some σ^0 values also holds for the corresponding $\sigma_R{}^0$ values of Taft, *et al.*; see the section on $\sigma_R{}^n$ values.

Yukawa, Tsuno, and Sawada's σ^0 Values. The authors mentioned[6d] derived most of their σ^0 values "directly" from the single reaction 3d, and these are in good agreement with our average σ^n values. The σ^0 values listed for 4-NH_2 and 4-NMe_2 (and 4-OH) were "derived from other reactivities statistically,"[6d] *i.e.*, by extrapolation of a plot of $\bar{\bar{\sigma}}$ *vs.* r^+ as shown for 4-NMe_2 (and OH) in Figure 7 of their paper.[17]

We do not believe that such a plot can give a reliable value of σ^0 of the substituents in question, because of the following cumulation of interlocking reasons. The slope of the line is relatively large; therefore, the intercept (σ^0) is strongly dependent on the values of r^+, in particular the lower ones; however, low values of r^+, quite generally, cannot be determined with the required accuracy (see below), and this holds especially for these cases where the more highly exalted values (NH_2, NMe_2) must not be used in the calculation.

Considering, specifically, only the two points for 4-NMe_2 with the lower r^+ values, these derive from the dissociation constants of benzoic acids in water (reaction 43; r^+ is given as 0.272), and from the "nonreactivity" nmr data on substituted 4-fluorobenzophenones (reaction 51;[18] r^+ given as 0.325). The uncertainties of such low r^+ values can be exemplified by noting that $r^+ = 0.3$ corresponds with $\sigma - \sigma^n \approx 0.2$ for 4-OMe (see below); in view of the variations found for both σ and σ^n (*cf.* Tables III and IV) this means an uncertainty in r^+ of 0.05 or more. As to the point referring to the benzoic acids, the σ^0 value of 4-NMe_2 was used[19] in calculating r^+, an approach that is mathematically incorrect. Apart from this, the dissociation constant used for 4-dimethylaminobenzoic acid, taken from the literature[20] and giving $(\Delta \log K)/\rho = \sigma = -0.83$,[20] is uncorrected for zwitterion and therefore certainly in error; the correct value is about -0.7.[21] It can be easily verified that numerical uncertainties like those indicated here may cause the extrapolated σ^0 value to be 0.2–0.3 unit in error; this also means, of course, that our σ^n values are not inconsistent with a plot of the type in question.

After the present paper had been submitted, we became acquainted with more recent work by Yukawa, *et al.*,[6e] containing a reexamination of the applicability and limitation of their set of σ^0 values. In their approach, "apparent" σ^0 values were calculated from the regression lines obtained on the basis of meta and para σ^0 values, including[22] that of 4-NH_2. The results were considered to confirm the validity of the original set.

In order to further examine the discrepancy for 4-NH_2 and 4-NMe_2, we have extended our calculations to regression lines based on $\sigma_m{}^n$ *and* $\sigma_p{}^n$, as well as on $\sigma_m{}^0$ *and* $\sigma_p{}^0$, with and without the inclusion of 4-NH_2 and 4-NMe_2.[23] This provides four different methods of calculation; for each of them apparent sigma values have been derived as σ, $\bar{\sigma}$, and $\bar{\bar{\sigma}}$. Of course, if the Hammett relation holds, and if the sigma values are correct, these apparent sigma values should be equal and equal to the input values.

Average values thus obtained for 4-NH_2 and 4-NMe_2 are listed in Table V; individual data are given in Tables X and XI in the Appendix.[10] When comparing data from the same sets of reactions it is seen that methods 1–4 give essentially the same results; the 4 reaction series used by Yukawa, *et al.*,[24] happen to give average values (for 4-NH_2) which are somewhat more negative than those of the 8 reaction series from Table II, but which do not approach the σ^0 values. When comparing the data of methods 4 and 5, it is found that the inclusion of σ^0 of 4-NH_2 (and 4-NMe_2) provides apparent sigma values which are considerably more negative but not as highly negative as the input values.

The above regularities and irregularities are as to be expected if our σ^n values of 4-NH_2 and 4-NMe_2 are essentially correct and Yukawa, *et al.*'s, σ^0 values are too highly negative. Further support for this contention comes from the following: (a) ρ values obtained with method 1 (ρ_m) are close to those from methods 2–4 (average difference 2%); method 5, however, gives ρ values which are 12 ± 2% lower; (b) all values of Δ^0 from method 5 are positive, and

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[15] The reasons for this adjustment are given in ref 5a, Table II, footnote *e*, and relate to internal consistency. Our treatment of reaction B.2 (Table II, footnote *g*) does not support this adjustment and indicates $\rho = 1.00$ to be low.

[16] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, **10**, in press. As to the ir data: *cf.* H. A. Lloyd, K. S. Warren, and H. M. Fales, *J. Amer. Chem. Soc.*, 88, 5544 (1966); as to reaction 13a: *cf.* ref 3 and W. Prikoszovich and H. Schindlbauer, *Chem. Ber.*, 102, 2922 (1969).

[17] Reference 6d; as to the definition of $\bar{\bar{\sigma}}$ see ref 9 of the present paper.

[18] This work, quoted as unpublished in ref 6d, has since appeared: R. G. Pews, Y. Tsuno, and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 2391 (1967).

[19] Reference 6d, Table V, footnote 48.

[20] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958); the original data are due to J. Johnston, *Proc. Roy. Soc., Ser. A*, 78, 103 (1906); *cf.* R. A. Robinson and A. I. Biggs, *Aust. J. Chem.*, **10**, 128 (1957).

[21] Based on a uv spectroscopic determination of pK_a and an estimation of zwitterion by comparison with methyl 4-dimethylaminobenzoate; *cf.* Robinson and Biggs.[20]

[22] The text of ref 6e suggests otherwise (*e.g.*, p 1203, first column), but the inclusion of the 4-NH_2 group can be inferred from the data in Table 4.

[23] We have excluded para groups with $-M$ effect (NO_2, CN, COMe) for reasons explained in ref 1 and in this paper. Inclusion of the available data does not impair our conclusions as to the amino groups.

[24] Yukawa, *et al.*,[6e] use the reactions 2a, 3a, 3b, and 5, and disregard 3c, which was considered to be inaccurate.[6d] We do use 3c, and, adding 1e, 4c, and 6b, have eight reaction series at our disposal. As to reaction 3b, we use only Kindler's data as specified in Table II; Yukawa, *et al.*,[6e] use reaction constants for H and 3,4-benzo which are due to A. Fischer, J. Packer, J. Vaughan, A. F. Wilson, and E. Wong, *J. Org. Chem.*, **24**, 155 (1959); *cf.* also Taft's treatment of the same reaction which is discussed in the text.

Table V. Average Sigma Values of 4-NH_2 and 4-NMe_2, as Calculated with Different Methods

Method	Basis sets of σ^a	4-NH_2				4-NMe_2			
		n^c	$-\sigma$	$-\bar{\sigma}$	$-\bar{\bar{\sigma}}$	n^d	$-\sigma$	$-\bar{\sigma}$	$-\bar{\bar{\sigma}}$
1a	σ_m^n Dippy; subst 1–10	8		0.25		3	0.24	0.25	0.24
		6	0.23	0.25	0.23				
		4		0.27		1	0.27	0.26	0.27
1b	σ_m^n Bolton;[b] subst 2, 3, 5, 6, 9	6	0.24	0.26	0.25	3	0.24	0.25	0.24
1c	σ_m^n Dippy; subst 2, 3, 5, 6, 9	6	0.23	0.25	0.24	3	0.24	0.25	0.24
2	σ_m^n and σ_p^n, excluding NH_2 and NMe_2	8	0.24	0.25	0.25	3	0.21	0.24	0.22
		7	0.26	0.27	0.27	2	0.22	0.24	0.22
		4	0.29	0.28	0.30	1	0.25	0.26	0.25
3	σ_m^n and σ_p^n, including NH_2 and NMe_2	8	0.24	0.25	0.24	3	0.22	0.24	0.23
		7	0.25	0.26	0.26	2	0.22	0.24	0.22
		4	0.27	0.27	0.28	1	0.23	0.25	0.23
4	σ_m^0 and σ_p^0, excluding NH_2 and NMe_2	8	0.26	0.26	0.26	3	0.23	0.24	0.23
		7	0.27	0.27	0.28	2	0.24	0.25	0.24
		4	0.30	0.28	0.31	1	0.26	0.26	0.26
5	σ_m^0 and σ_p^0, including NH_2 and NMe_2	8	0.31	0.28	0.31	3	0.29	0.27	0.28
		7	0.32	0.30	0.33	2	0.29	0.28	0.31
		4	0.34	0.31	0.35	1	0.32	0.30	0.33
6[e]	Extrapolation $(\Delta \log K)/\rho$ *vs.* r^+				0.36				0.48

[a] The substituents actually used are specified in Table II (method 1a), and Tables VIII[10] and IX[10] (methods 2–5). [b] Reference 28. [c] Number of reactions; $n = 4$: reactions 2a, 3a, 3b, 5 (*i.e.*, the reactions used by Yukawa, *et al.*,[6e]); $n = 8$: reactions added 1e, 3c, 4c, 6b; $n = 7$: reaction 3c excluded (as by Yukawa, *et al.*,[6d,e]); $n = 6$: reactions 2a and 3b excluded. [d] Number of reactions; $n = 3$: reactions 1e, 3c, 5; $n = 2$: reaction 3c excluded; $n = 1$: reaction 5. [e] Reference 6d.

each is more positive than the corresponding one from method 4 (av 0.027 and 0.009, respectively); (c) the the values of s and R are better with method 3 (σ^n) than with method 5 (σ^0); for 8 reaction series: av s = 0.029 and 0.040, av R = 0.991 and 0.983, respectively; (d) in series lacking amino derivatives, σ^n gives somewhat better correlations than σ^0. Relevant details are listed in Tables VIII and IX in the Appendix.[10]

It will be observed that s and R as given by Yukawa, *et al.*,[6d,e] are often better than ours. This is due to their deleting data which do not adhere well; this holds, *e.g.*, for both Table 4[25] and Table 5[26] of ref 6e. Similarly, several apparent σ^0 values are not used when averaging.[27] From these and other details the impression is gained that the authors have considerably more faith in adherence to the Hammett equation than we have. We carry the third decimal of σ values for arithmetic purposes; we accept large variations in the second decimal when varying reaction series and solvent; we are hopeful as to the interpretation, in related systems, of differences of 1 unit in the first decimal.

Table V also gives some results of calculations based on the σ_m values of the substituents 2, 3, 5, 6, and 9, due to Bolton, *et al.*,[28] which came to our attention after submitting the present paper. The corresponding ρ_m values are 1–4% lower, and sigma values are slightly more negative. The conclusions of our work are not affected.

The above comments on data from the literature imply that we do regard the average σ^n values of 4-NH_2 and 4-NMe_2 (and OH) given in Table IV as the ones to be preferred. One piece of evidence can be added. In part I[3] we calculated through-resonance energies (ΔG_p) of 4-alkoxycarbonylanilines from their basic strengths; then, accepting the transition state of the alkaline hydrolysis of these esters to have no through-resonance interaction, we calculated σ^n of the amino groups from the σ value observed in the ester hydrolysis. Repeating this procedure with new data,[29] we obtain σ^n-4-NMe_2 = −0.26 as an average of two values, and σ^n-4-NH_2 = −0.26 as an average of five values, supporting the values from reactions 1–10.

As noted above, the difference between σ^n values from insulated and noninsulated systems is reassuringly small for +M substituents; accordingly, (weighted) averaging of these values might be suggested. We have not done so since we have some preference for the data derived in the present paper as based on more recent, more homogeneous measurements.

$\Delta\sigma_R^+$ Values; the Yukawa–Tsuno Equations. The heart of the Yukawa–Tsuno equations[6,7] is the linear relation between the exaltations of σ in different reactions. For +M substituents this relation can be written as

$$\sigma - \sigma^n = r^+(\sigma^+ - \sigma^n) \equiv r^+\Delta\sigma_R^+ \qquad (2)$$

where: σ = observed σ value; σ^+ = observed σ value for a standard reaction, chosen as the S_N1 reaction of $ArCMe_2Cl$ in 90% acetone at 25°; $\Delta\sigma_R^+$ = standard exaltation of σ; r^+ is a proportionality factor; $r^+ \equiv 1$ for the standard reaction. Equation 2 leads to the extended Hammett equation

$$\log K - \log K^0 = \rho\sigma^n + \rho r^+\Delta\sigma_R^+ \qquad (3)$$

We regard the Yukawa–Tsuno treatment as a substantiated improvement in the description of substituent effects. It provides a quantification of the multiplicity of σ values (and $\Delta\Delta G_p$) discussed in part I of this series,[3] r being a measure of the relative degree

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(25) In Table 4, 133 data are available (not counting 3-OMe, 3-I, and 4-I), 12 data are not used. If, for instance, in reaction 8 (our no. 5), 4-NMe_2 is not deleted, s increases from 0.012 to 0.037, and R decreases from 0.999 to 0.989. Similar remarks apply to a recent paper by L. A. Cohen and S. Takahashi, *J. Amer. Chem. Soc.*, **95**, 443 (1973).

(26) From Table 5 values are missing for reaction 3: 4-NO_2 (0.96 is our σ value); 4: 4-CN (0.57), 4-*i* Pr (0.36); 7: 4-*t*-Bu (0.05); 8: 4-NMe_2 (−0.27); 10: 4-CN (0.79); 13: 4-OMe (−0.23).

(27) See footnote *e* of Table 5. For 4-OMe, three values out of 12; for 4-F, three values out of eight.

(28) P. D. Bolton, K. A. Fleming, and F. M. Hall, *J. Amer. Chem. Soc.*, **94**, 1033 (1972).

(29) ΔG_p of methyl and ethyl 4-aminobenzoate, −1.2 kcal/mol; of 4-dimethylaminobenzoates, −1.5 kcal/mol. The ester hydrolyses were reactions 46, 47, and 50 of ref 3, from which the ρ- and σ-amino values were taken.

of the exaltation of σ values in a reaction series, and its variation corresponding to multiplicity of σ. Accordingly, we have used the equations and extended upon them in recent papers.[1,2]

On the other hand, it should be borne in mind that eq 2 is possibly not of high precision and that experimental proof is scarce and difficult to provide. Even if the "intrinsic linearity" were correct, the limitations of the Hammett equation, the (differential) variation of σ and σ^n with solvent, etc., prevent a proper check, especially for lower values of r^+ (*cf.* the above discussion of σ^0). A few examples would seem appropriate.

In Figure 5 of ref 6b, the filled circles show a frequently occurring situation: one point (4-OMe) well away from both axes and an irregular "cluster" of points near the origin. This is a relatively favorable plot because both r^+ values are high (0.7 and 1.0), but it contributes little evidence as to linearity; the points near the origin are too uncertain for that. Of course, the slope is almost entirely determined by the point for 4-OMe, so that adherence to eq 3 is good, but adherence to eq 3 is, in this case, a poor test of eq 2. Figure 9 of ref 6c demonstrates the same situation in another way. Neither σ nor σ^+ is satisfactory, and $r^+ = 2.29$ provides the best fit to eq 3; for that r^+ value 4-OMe is close to the regression line, but 4-F is "overcompensated" and deviates more than with σ^+.

A good check of linearity requires a wide range of $\Delta\sigma_R{}^+$ which is well distributed, including, *e.g.*, 4-OMe *and* 4-NMe$_2$. The open circles of Figure 5 of ref 6b provide such an example and present a satisfactory linear behavior. Figure 6 of ref 6c also carries some weight, as do some other related reactions.[30]

The above restrictions in testing eq 2 are not removed by the use of σ^n values. An important factor is that the ratio of the $\Delta\sigma_R{}^+$ values of, *e.g.*, 4-OMe and 4-NMe$_2$ is changed very little (see Table IV). Therefore, no attempt will be made here to reevaluate the data pertaining to eq 2.

We have recalculated $\Delta\sigma_R{}^+$ values using the average σ^n values of Table IV as follows. Retaining the standard reaction (ArCMe$_2$Cl), the relevant σ values calculated in part I,[3] reaction 1010, were taken as "primary" σ^+ values. Most of the other $\Delta\sigma_R{}^+$ values stem from σ values calculated in part I for reaction 1006 ($Ar_3COH \rightleftarrows Ar_3C^+$), $\sigma - \sigma^n$ being brought to the standard scale through the value of $\Delta\sigma_R{}^+$ − 4-OMe = −0.71 only, *i.e.*, by calculating r^+ from the data on 4-OMe and assuming eq 2 to be applicable. The remaining values were calculated similarly, as indicated in Table IV. This procedure was preferred over that used by Yukawa and Tsuno,[6b] since the data for reaction 1006 were considered to be more reliable than those for the other reactions used by them. Also, in their work a substantial number of the available data were omitted or were replaced by those from related reactions, suggesting a better adherence to eq 2 than is actually obtained.

The σ^+ values, given in the last column of Table IV, are given only for comparison with earlier data.

$\sigma_R{}^n$ Values. The normal σ values have been further dissected by Taft, *et al.*, in contributions of inductive (σ_I) and resonance effects ($\sigma_R{}^0$).

$$\sigma^0 \equiv \sigma_I + \sigma_R{}^0 \qquad (4)$$

In our notation

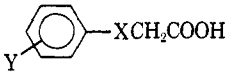
$$\sigma^n \equiv \sigma_I + \sigma_R{}^n \qquad (5)$$

Taft, *et al.*,[5] primarily derived $\sigma_R{}^0$ values, and obtained σ^0 by using their σ_I values; we derive σ^n directly and can obtain $\sigma_R{}^0$ by using σ_I values. Since the objections raised above against several of Taft's σ^0 values apply equally (in fact primarily) to $\sigma_R{}^0$ values, a reexamination would seem to be in order.

Combination of σ_I values of Taft, *et al.*,[31] with our σ^n values gives, for some important substituents, the following values of $\sigma_R{}^n$: 4-NH$_2$, −0.34; NMe$_2$, −0.34; OH, −0.37; OMe, −0.34; O$^-$, −0.4[32]; F, −0.34; Cl, −0.18; SMe, −0.10; Br, −0.15; NHAc, −0.14; OPh, −0.29; Me, −0.05.

The most important and intriguing generalization is that, in contradistinction with listed $\sigma_R{}^0$ values, simple first-row substituents (O$^-$ included[32]) have essentially identical $\sigma_R{}^n$ values of about −0.35.[33] A similar observation has been made by McKeever and Taft[34] with respect to substituent effects in trityl anions. A qualitative explanation can be advanced on the basis of the I_π effect[35] and/or Mulliken's suggestion[36] concerning the relation between mesomeric and inductive effects; in addition, differences in hybridization, in solvation, and in semicyclic bond distances should be taken into account. Whatever the detailed explanation may turn out to be, the above data justify considerable reservations regarding current $\sigma_R{}^0$ values and any of their correlations with other quantities.

−M Substituents. In the accompanying study[1] of the dissociation constants of compounds of the type



with X = NH, O, and CH$_2$, we found σ-4-NO$_2$ to be exalted, $\Delta\Delta G_p$ being proportional to $\Delta\sigma_R{}^+$ of X-CH$_3$. For 4-CN the values of $\Delta\Delta G_p$ are smaller in a proportion corresponding with the $\Delta\sigma_R{}^-$ values of 4-NO$_2$ and 4-CN, as required by the Yukawa–Tsuno equation for − M substituents.[1,7]

$$\sigma - \sigma^n = r^-(\sigma^- - \sigma^n) \equiv r^-\Delta\sigma_R{}^- \qquad (6)$$

Furthermore, lengthening the side chain (X = NHCH$_2$) as well as shortening it (ArNHNH$_3{}^+$) left the exaltation of σ of the 4-nitro group almost unchanged, and an explanation of this result was presented. In harmony with this, we now find exaltations in the arylacetic

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(30) C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 297 (1961); C. Eaborn and J. A. Waters, *ibid.*, 542 (1961); R. Baker, R. W. Bott, C. Eaborn, and P. M. Greasley, *ibid.*, 627 (1964). The data in Figure 6, ref 6c, are from C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

(31) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 85, 722 (1963). Slightly different σ_I values are given in other papers, but using these would not alter the conclusions of this section.

(32) We give this figure with hesitation, since σ^n has been obtained indirectly (see Table IV), and since other poles behave abnormally (see our data for positive poles, Table III).

(33) *Cf.* ref 3, pp 842–843.

(34) L. D. McKeever and R. W. Taft, *J. Amer. Chem. Soc.*, 88, 4544 (1966).

(35) See, *e.g.*, J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," 2nd ed, Wiley, London, 1970, p 325; P. Politzer and J. W. Timberlake, *J. Org. Chem.*, 37, 3557 (1972).

(36) R. S. Mulliken, *Tetrahedron*, 5, 253, 270 (1959); *cf.* ref 5b, p 5360, and ref 34.

Table VI. $-$M Substituents; Summary of Para σ Values:[l] σ^n, σ^0, $\Delta\sigma_R^-$, σ^-

Sub- stituents	σ^n and average σ values					Taft,[c]		
	This paper[a]			Part I[b]				
	σ	n	$\bar{\sigma}$	σ	n	σ^0	$\Delta\sigma_R^{-\,d}$	$\sigma^{-\,e}$
CHO	**0.43**[g]			0.23[g]			0.55	0.98[k]
COMe	**0.502**[h]			**0.502**[h]		0.46	**0.32**	0.82
	0.51 ± 0.02	2	0.51			0.40		
CN[f]	**0.70**[i]			0.67	5	0.69	**0.29**	0.99
	(1) 0.77 ± 0.06	12	0.73			0.63		
	(2) 0.79 ± 0.03	7	0.75					
	(3) 0.74 ± 0.07	5	0.72					
$CONH_2$	**0.31**[i]						**0.31**	0.62
COOH				**0.41**	3			
COOMe	**0.46**[i]			0.48[j]	1	0.46	**0.28**	0.74
COOEt				**0.44**	5			
CF_3				**0.53**	3			
NO_2[f]	**0.778**[h]			**0.778**[h]		0.82	**0.45**	1.23
	(1) 0.83 ± 0.09	20	0.81			0.73		
	(2) 0.91 ± 0.04	8	0.87					
	(3) 0.77 ± 0.07	12	0.77					
SO_2Me	**0.73**[i]			0.69	1		**0.32**	1.05
SO_2NH_2				**0.59**	3			

[a] Standard σ values and average σ values, with their standard deviation, for reactions 1–10; n, number of data; $\bar{\sigma}$, average $\bar{\sigma}$ value. [b] Reference 3. [c] Reference 5c. [d] $\Delta\sigma_R^- = \sigma^- - \sigma^n$. [e] Observed σ value for the dissociation constants of anilinium ions in water at 25°; unpublished work by A. G. N. Boers. As far as they can be compared, these data are in good agreement with published data. [f] 1, all values; 2, σ values from pK_a* of acids (reactions 1, 4, and 6); 3, other values. [g] A. A. Humffray, J. J. Ryan, J. P. Warren, and Y. H. Yung, *Chem. Commun.*, 610 (1965). The σ^n value of 4-CHO = 0.23 from ethyl benzoate hydrolysis (ref 3, reaction 47j) is probably in error, as discussed by the authors mentioned. [h] Standard σ value, from data by Dippy, *et al.*, on benzoic acids in water at 25° (*cf.* ref 3). [i] From unpublished measurements by A. G. N. Boers and A. J. Hoefnagel on benzoic acids in water at 25°. [j] The figure given in ref 3 is in error: for reaction 11 the σ values listed for 3- and 4-COOMe pertain to 3- and 4-OCOMe. Accordingly only this one σ^n value remains. [k] Reference 3. [l] Preferred values are in boldfaced type.

acids, larger for 4-NO_2[37] than for 4-CN, and comparable with those in the β-arylpropionic acids (X = CH_2). For reaction series 1, 4, and 6, the eight values for σ-4-NO_2 range from 0.86 to 0.98 (σ^n = 0.78), with an average of 0.91;[40] the seven values for 4-CN range from 0.76 to 0.85 (σ^n = 0.70) with an average of 0.79.[41] Again, the effect of the steric inhibition of resonance, as in 3,5-dimethyl- and 3-*tert*-butyl-4-nitrophenylacetic acid, is similar to that in the previous study.

A much less consistent picture emerges when the other reaction series are considered. For σ-4-NO_2 the 12 values range from 0.67 (reaction 2a) to 0.86 (reactions 3c, 7, and 10), with an average of 0.76. The five values of σ-4-CN range from 0.66 to 0.84, with an average of 0.74. Part of these variations can possibly be ascribed to a solvent dependence[42] of σ and of the hyperconjugation involved, as also to steric hindrance to solvation. Differences in conformational preference might play a role as between those depending on the anions of the acids with planar carbon, and the transition states of ester hydrolysis with tetrahedral carbon as the center of a very bulky negatively charged group. From the experimental point of view it is vexing that the data for reactions 3c and 3d, in the same solvent, give σ-4-NO_2 as 0.86 and 0.81, respectively, suggesting a behavior similar to and different from, respectively, the arylacetic acids. If Yukawa and Tsuno[6d] are right in believing their data (reaction 3d) to be the more accurate, it remains to be explained why the correlation with the arylacetic acids is not satisfactory with respect to the data of the 4-NO_2 derivatives.[37] The interpretation of these discrepancies has to await further experimental and theoretical work.

The present paper and the previous one[1] cast doubt on the reliability of σ^n values of $-$M substituents as derived from any system insulated by alkylene groups, and the acid dissociation constants have certainly been shown to be unsuitable, having a Yukawa–Tsuno proportionality constant $r^- \approx 0.3$. These σ^n values are best obtained from $-$M,$-$M combinations, as in the benzoic acids. Table VI contains a summary, and also $\Delta\sigma_R^-$ and σ^- values used in the present and in previous papers.[1,2]

With respect to the σ^n values of +M substituents, we have no indications that the insulated systems are suspect. For the σ^n values of ±M substituents (Ph, SMe), the insulated systems are, of course, the only choice.

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(37) The pK_a of 4-nitrophenylacetic acid was given as 3.85 by Dippy, *et al.*,[38] who also observed and discussed its anomaly with respect to 3-nitrophenylacetic acid, and as 3.92 by Fischer, *et al.*[39] From correspondence with Dr. Vaughan (Dec 19, 1963) we quote the following statement in the thesis of B. R. Mann: "In the calculation of the dissociation constant for this acid, λ [conductance] and the pressure variation of λ for the potassium salt of the acid were taken as the mean values for the salts of the other phenylacetic acids (potassium *p*-nitrophenylacetate was insufficiently soluble in water to allow conductance measurements to be made)." As Dippy, *et al.*, report a value of λ which deviates from the average, we disregarded the pK_a given by Fischer, *et al.*, in the present work. We note that the difference between our pK_a, 3.89, and that of Dippy, *et al.*, is much larger than usual. With both these values, however, the correlation between the pK_a of arylacetic acids and the rate constants of alkaline hydrolysis of their ethyl esters as observed by Yukawa, *et al.*,[6d] is less satisfactory than assumed by these authors, who used the datum of Fischer, *et al.* (see ref 6d, Figure 1).

(38) J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 161, 1888 (1934); J. F. J. Dippy, H. B. Watson, and F. R. Williams, *ibid.*, 346 (1935); J. F. J. Dippy and R. H. Lewis, *ibid.*, 644 (1936); J. F. J. Dippy and J. E. Page, *ibid.*, 357 (1938); J. F. J. Dippy, *Chem. Rev.*, 25, 151, 175 (1939).

(39) A. Fischer, B. R. Mann, and J. Vaughan, *J. Chem. Soc.*, 1093 (1961).

(40) In terms of ref 2, these data mean that $\Delta\sigma_R^+(CH_2COOH) - \Delta\sigma_R^+(CH_2COO^-) \approx 0.1$.

(41) On the basis of σ_m values due to Bolton, *et al.*,[28] the average values are 4-NO_2, 0.95 and 4-CN, 0.82. With the σ_m values due to Dippy for the same substituents, these averages are 0.92 and 0.80, respectively.

(42) See N. B. Chapman, *et al.*, Table II, footnote *e*.

Experimental Section

Some data on preparation, melting point, and elemental analysis of the compounds studied are given in the microfilm edition[10] of this volume of the journal.

Dissociation Constants. The thermodynamic pK_a* values were determined using the method described by van Veen, *et al.*[43] Part III of this series[1] provides some details as to calculation and precision, and also a discussion of the correction of the "overall" pK_a* values of the amino acids for the presence of ammoniocarboxylic acid and/or zwitterion.

Methyl 4-aminophenylacetate hydrochloride was obtained by treating a solution of the amino ester in ether with dry hydrochloric acid gas: mp 189–191° (C, H, and N analyses were correct); pK_a* in 50% ethanol, 3.89.

Acknowledgments. The authors thank: A. G. N. Boers for allowing them to use and quote some of his unpublished data; R. O. C. Norman and D. J. Byron for the determination of several rate constants; R. W. Taft and S. Ehrenson for pleasant contacts and for permission to quote from an unpublished paper; H. van Bekkum and J. G. Watkinson for some samples; M. van Leeuwen for carrying out the elemental analyses; and M. A. Hoefnagel for the preparation of some compounds.

This paper and parts II and III of this series were composed at the University of California at Santa Cruz while B. M. W. was on sabbatical leave. Thanks are due to J. F. Bunnett for kind hospitality and thoughtful discussions.

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(43) A. van Veen, A. J. Hoefnagel, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **90**, 289 (1971).

Crystal Structure of 2,2,3,3,4,4-Hexafluoro(triphenylphosphoranylidene)cyclobutane

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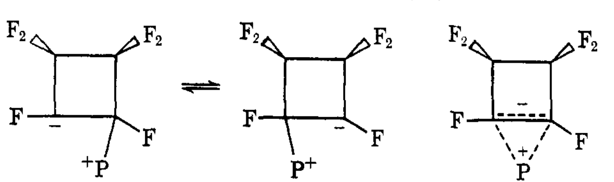
Abstract: 2,2,3,3,4,4-Hexafluoro(triphenylphosphoranylidene)cyclobutane ($(C_6H_5)_3PC_4F_6$) crystallizes in the triclinic space group, $P\bar{1}$, with cell parameters $a = 9.571\ (13)$ Å, $b = 10.478\ (5)$ Å, $c = 11.189\ (5)$ Å, $\alpha = 116.85\ (3)°$, $\beta = 93.46\ (18)°$, $\gamma = 96.40\ (18)°$, $Z = 2$. The observed and calculated densities are 1.46 (3) and 1.432 g/cm^3. Intensity measurements were made on a Picker four-circle automatic diffractometer. A total of 2558 independent reflections were fitted by least-squares methods to a molecular model with $R_2 = 0.046$. The molecular configuration of the compound was found to be that of the ylide structure. The phosphorus atom has four neighbors at essentially tetrahedral angles. The phosphorus–ylide carbon bond length is 1.713 (3) Å (compared with C=P of 1.665 Å and C—P of 1.828 Å). The phosphorus atom is coplanar with the cyclobutane ring. The carbon–fluorine bond lengths are slightly longer than those in perfluorocyclobutane with the exception of the carbon(3)–fluorine(3) bond.

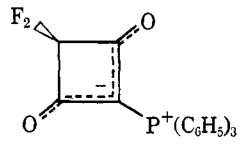
Stockel, Megson, and Beachem reported isolation of a 1:1 adduct when triphenylphosphine and perfluorocyclobutene were allowed to react in anhydrous ether solvent.[1] The structure postulated was either a 1,3-dipolar species (I) which underwent rapid equilibration in solution or a nonclassical structure (Ia).



I Ia

Rapid equilibration accounted for the ^{19}F nmr spectrum which showed a symmetrical multiplet due to four chemically equivalent fluorines at ϕ 86.1 and a symmetrical multiplet at ϕ 124.2 due to two equivalent fluorines.

The 1,3-dipolar structure seemed unlikely due to the ease of carbanions to eliminate a β-fluoride ion. Also, mechanistic consideration of the hydrolysis reaction of this 1:1 adduct leading to the ketobetaine type ylide (II) indicated that nucleophilic attack by



II

water occurred on the cyclobutane ring. This would be unlikely on the basis of the proposed structure.

Repetition of the reaction of triphenylphosphine with perfluorocyclobutene in our laboratories resulted in the isolation of a compound with identical properties with those reported previously.[1] Although the possibility of a 1,3-dipolar structure was readily eliminated, the structures III, IV, and V are possible.

All these structures would be expected to belong to the same nuclear spin system, $A_2A_2'MM'X$. Due to the unique nature of IV and V, it was thought that a computer programmed analysis of the ^{19}F nmr spectrum would not comprise conclusive proof of the identity of this compound. Therefore, a complete

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(1) R. F. Stockel, F. Megson, and M. T. Beachem, *J. Org. Chem.*, 33, 4395 (1968).