B. (6 Equiv of 1-Butynylcopper, 70–80°). The above reaction was repeated using III (5 g, 0.0131 mol), 1-butynylcopper (9.21 g, 0.079 mol), and pyridine (180 ml) in the indicated quantities. Separation as previously described and chromatography of the products on acid-washed alumina with Skellysolve B gave XXVIb (~0.47 g, 0.001 54 mol, 12%) and then IIb (a yellow oil, 1.92 g, 0.00827 mol, 63%). The diacetylene exhibits infrared absorption at 4.47 μ (C≡C), nuclear magnetic resonance at τ 8.8 (triplet, 3 H), 7.6 (quartet, 2 H), and 2.7 (multiplet, 3 H), and a parent mass spectral peak at 232.2.

Diacetylene IIb was converted to its monopicrate as follows. Solutions of picric acid (0.40 g, 0.00175 mol) and of IIb (0.4 g, 0.00173 mol) in warm 95% ethanol (8 ml) were mixed. On standing orange needles of the monopicrate of IIb precipitated (0.42 g, 9.1 × 10⁻⁴ mol, 53%), mp 133–134° (from 95% ethanol).

Anal. Calcd for $C_{24}H_{19}N_3O_7$: C, 62.47; H, 4.12; N, 9.11. Found: C, 62.31; H, 4.05; N, 9.29.

Reaction of 1,8-Diiodonaphthalene (III) and 1-Hexynylcopper. A mixture of III (5.0 g, 0.031 mol), 1-hexynylcopper[27] (11.41 g, 0.0786 mol), and dry pure pyridine (150 ml) was stirred at 80° for 24 hr in a nitrogen atmosphere. Concentration, chromatography, and puri-

fication of the products as in the previous experiments yielded impure 8-iodo-1-(1-hexynyl)naphthalene (XXVIc)[28] and 1,8-bis(1-hexynyl)naphthalene (IIc, 1.46 g, 0.00506 mol, 39%[28b]) as a light yellow oil. Nuclear magnetic resonance occurs in IIc at τ 9.0 (distorted triplet, 3 H), 8.4 (multiplet, 4 H), 7.5 (distorted triplet, 2 H), and 2.6 (multiplet, 3 H). The ratio of aliphatic to aromatic hydrogen found for IIc is 3.05, theory 3.00.

Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.15; H, 8.34.

(27) Prepared by addition of 1-hexyne (20.5 g, 0.25 mol) in 95% ethanol (80 ml) to a solution of cuprous chloride (54.4 g, 0.55 mol), water (200 ml), and concentrated ammonium hydroxide (200 ml).

(28) (a) In reaction of III with 2 equiv of 1-hexynylcopper at room temperature for 72 hr, the principal product is XXVIc. It is difficult to separate XXVIc from III and IIc. The structure of XXVIc is assigned from its acetylenic absorption at 4.4–4.5 μ, its nearly acceptable analysis and its nuclear magnetic resonance at τ 9.1 (distorted triplet, 3.1 H), 8.5 (multiplet, 4.5 H), 7.6 (multiplet, 2 H), and 2.5 (multiplet, 6.2 H). The ratio of aliphatic to aromatic hydrogen observed in XXVIc is 1.54, theory 1.50. (b) The yield of IIc is considerably higher than reported because of the difficulty in its separation from XXVIc.

Nuclear Magnetic Resonance Studies of *ortho*-Substituted Phenols in Dimethyl Sulfoxide Solutions. Electronic Effects of *ortho* Substituents[1]

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Abstract: The relative chemical shifts of OH in *ortho*-substituted phenols ($\Delta\delta_o$) in dimethyl sulfoxide (DMSO) solutions are linearly related to those for *para*-substituted phenols ($\Delta\delta_p$), are apparently free of steric effects, and afford an excellent measure of electronic effects of *ortho* substituents. The strong intermolecular hydrogen bond between the phenolic OH and DMSO is apparently oriented away from a single *ortho* substituent so that proximity interactions are minimal; 2,6-disubstituted phenols do exhibit serious steric interactions even in DMSO solution. The $\Delta\delta_p$ values are linearly correlated with Hammett σ_p^- constants, and, from the equation for this line ($\sigma^- = 0.720\Delta\delta - 0.038$) *ortho*-substituent constants (σ_o^-) for 32 substituents have been assigned. The *o*-acetyl and *o*-nitro substituents do not fit this correlation because of intramolecular hydrogen bonding. The new *ortho*-substituent constants are shown to correlate successfully the reactivity data for *ortho*-substituted compounds in 29 reaction series.

A well-known observation by investigators in the field of physical organic chemistry concerns the inability of the classical Hammett σ–ρ approach[2] (eq 1) to corre-

$$\log (k/k_0) = \sigma\rho \tag{1}$$

late rate or equilibrium data for *ortho*-substituted benzene derivatives. Discussions of linear free energy relationships with particular emphasis upon the Hammett equation have been the subject of several recent reviews.[3]

Although to date theoretical and empirical studies of rate and equilibrium data have been generally unsuccessful in describing the reactivities of *ortho*-substituted compounds accurately, for some time chemists have had at their disposal the knowledge of some of the various interactions which may occur between the *ortho* substituent and the reaction center (including its solvation sheath). Some of the more important phenomena which may substantially affect reaction rates of *ortho*-substituted benzene derivatives are (1) both intra- and intermolecular hydrogen bonding; (2) substituent polar interactions transmitted to the reaction center either through the σ-bond network (inductive effect[4]) or more

(1) (a) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10, 1967, Abstracts S89, and at the Second Conference on Linear Free Energy Relationships, University of California, Irvine, March 27–29, 1968; (b) abstracted from the Ph.D. dissertation of M. T. T., submitted to Louisiana State University, May, 1968.

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

(3) (a) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); (b) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964); (c) C. D. Ritchie and W. F. Sager, *ibid.*, **2**, 323 (1964); (d) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963);

(e) V. Pal'm *Russ. Chem. Rev.*, **9**, 471 (1961); *Uspekhi Khim.*, **30**, 1069 (1961); (f) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter XIII.

(4) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941: (a) pp 192–194; (b) pp 258–259.

directly through space (field effect[5]) and resonance interactions transmitted primarily through the π-bond network;[6] and (3) steric interactions between the *ortho* substituent and the ground- or transition-state configuration of the reaction center.[7] Since these interactions are often linked, mathematical separation of *ortho* interactions, which may alter the linear free energy relationship through nonlinear changes in the entropy terms,[2] is often a difficult and unrewarding task.

Previous attempts in describing the reactivities of *ortho*-substituted compounds have met with only limited success. There is to date no unambiguous mathematical description either of electronic effects of *ortho* substituents in the absence of proximity interactions or of the proximity interactions themselves. We believe that we have resolved at least part of the problem connected with *ortho* substituents by determining *ortho*-substituent constants in a system which, through a fortuitous effect of solvation, is apparently free from almost all proximity interactions. This system, consisting of a solution of an *ortho*-substituted phenol in dimethyl sulfoxide (DMSO) solvent, is responsive to electronic effects from the substituents as measured by the nuclear magnetic resonance (nmr) chemical shift of the strongly intermolecularly hydrogen-bonded phenolic proton.

Thirty-two *ortho*-substituted phenols have been examined with respect to the Hammett relationship in order to relate the polar effect of the *ortho* substituent to that of the corresponding *para* one, to identify any steric effects operating in this system, to relate quantitatively the polar effects of *ortho* substituents to the Hammett scale, and to elucidate the inductive and resonance contributions to the polar effect of *ortho* substituents. The results indicate that effects of *ortho* substituents, in the absence of complicating factors, parallel closely those of the *para* substituents. Hammett σ_0^- values have been assigned to the 32 *ortho* substituents, the largest group of *ortho* substituents ever included in a single study of this type, and some interesting insights into the make-up of inductive and resonance contributions to the *ortho* substituent constant have been gained.

I. *meta*- and *para*-Substituted Phenols in DMSO Solution

The correlation of Hammett substituent constants with various physical properties and spectral parameters in substituted benzene derivatives has been extensively investigated in the last few years, and correlations of nmr absorptions with these substituent parameters have been particularly successful.[8,9]

Recent studies of *meta*- and *para*-substituted phenols in DMSO solution have demonstrated a linear correlation of the hydroxyl chemical shift with Hammett σ^- values.[9a,b] DMSO was chosen for these and the present study for several reasons, the most important one being that in this solvent the phenolic hydroxyl chemical shift is independent of concentration due to almost exclusive intermolecular hydrogen bonding between the OH group and DMSO.[10,11] In the absence of concentration dependence, direct chemical-shift measurements can be made without the necessity of extrapolation to infinite dilution. Electron-withdrawing substituents deshield the hydrogen-bonded OH–DMSO moiety, and the downfield chemical shift relative to phenol is designated as a positive $\Delta\delta$ value. Conversely, electron-donating substituents cause an upfield shift, designated as a negative $\Delta\delta$ value. The range of hydroxyl chemical shifts is about 150 Hz. The unique properties of the solvated hydroxyl group in this system enable the unambiguous observation of effects transmitted from the ring. Not only is the hydroxyl proton absorption located downfield to the extent that it is no longer in the region of normal proton absorptions,[11,12] but also the chemical shift acts as a sensitive probe to the transmission of electronic effects, as measured by the Hammett substituent constants.

In order to permit direct comparison of different nmr data obtained in a single study, the hydroxyl chemical shifts of 6 *meta*- and 30 *para*-substituted phenols were obtained in DMSO solution and are listed in Table I. Some of these data have been reported previously.[9a,b]

These hydroxyl chemical shifts were then compared with several sets of σ constants to determine the best description of the data.[13] For the *para* substituents no correlation was found between the relative hydroxyl chemical shift ($\Delta\delta$) and σ_I, σ_R, σ_R^0,[15] or σ_R^-.[9d] The standard σ values of McDaniel and Brown[16] give only a poor correlation ($r = 0.932$, $s = 0.155$, $n = 32$) while the σ^0 values of Taft[17] give a better fit with the data ($r = 0.966$, $s = 0.095$, $n = 18$). For the same 18 substituents, σ^- gives a similar correlation ($r = 0.974$, $s = 0.122$, $n = 18$). Because of this high correlation coefficient and

(5) (a) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 6, 506, 513 (1938); (b) F. H. Westheimer and M. W. Shookhoff, *J. Am. Chem. Soc.*, 61, 555 (1939).

(6) Other electronic mechanisms have been postulated [M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, 84, 3539 3548 (1962); M. J. S. Dewar and A. P. Marchand, *ibid.*, 88, 3318 (1966)]. These other interactions are usually of little importance, however, when compared to σ inductive, field, and π resonance effects [C. G. Swain and E. C. Lupton, Jr., *ibid.*, 90, 4328 (1968)].

(7) (a) D. A. D. Jones and G. G. Smith, *J. Org. Chem.*, 29, 3531 (1964); (b) N. B. Chapman, M. G. Rodgers, and J. Shorter, *J. Chem. Soc., B*, 157 (1968).

(8) For a summary of the literature concerning the investigations of absorptions by NH_2 in substituted anilines, CH_3 in *N,N*-dimethylanilines, OCH_3 in anisoles, CH_3 in toluenes, CHO in benzaldehydes, and $C\equiv CH$ in substituted phenylacetylenes, see I. D. Rae and L. K. Dyall, *Australian J. Chem.*, 19, 835 (1966).

(9) Absorptions by OH in substituted phenols: (a) J. G. Traynham and G. A. Knesel, *J. Org. Chem.*, 31, 3350 (1966). An erroneous σ for 3,4-dimethyl was tabulated in this paper. We thank Dr. B. M.

Lynch for calling this error to our attention. (b) R. J. Ouellette, *Can. J. Chem.*, 43, 707 (1965); (c) V. F. Bystrov, V. V. Ershov, and V. P. Lezine, *Opt. Spectry.* (*USSR*), 17, 290 (1964); *Opt. i Spektroskopiya*, 17, 538 (1964); (d) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, 85, 3402 (1963).

(10) For an extensive review of DMSO and its properties, see D. Martin, A. Weise, and H.-J. Niclas, *Angew. Chem. Intern. Ed. Engl.*, 6, 318 (1967).

(11) O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, 86, 1256 (1964).

(12) M. W. Dietrich, J. S. Nash, and R. E. Keller, *Anal. Chem.*, 38, 1479 (1966). These authors reported that, out of 14 solvents of varying polarities, only pyridine, trimethyl phosphate, and hexamethylphosphoramide (HMPA) surpass DMSO in shifting the hydroxyl nmr absorption of 2,6-dimethylphenol downfield. HMPA was used for the more inclusive study of phenol chemical shifts, and the data closely parallel those reported in the present paper for DMSO solutions.

(13) (a) The σ values used in this paper are from Ritchie and Sager[3c] unless otherwise designated. (b) The correlation coefficients (r) here and elsewhere in this paper (unless otherwise noted) are well within the acceptable standard of $r = 0.96$ set by Jaffé.[3a] In the list of statistical data for the forthcoming correlations, the following sequence will be observed: [correlation coefficient (r), standard deviation (s), number of substituents (n)]. Statistical calculation formulas are those of Snedecor.[14]

(14) G. W. Snedecor, "Statistical Methods," 4th ed, Iowa State College Press, Ames, Iowa, Chapters VI, XIII.

(15) R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, 90, 1757 (1968).

(16) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).

(17) R. W. Taft, Jr., *J. Phys. Chem.*, 64, 1805 (1960); see also ref 3c, pp 336–337.

Table I. Nmr Chemical Shift Data and Substituent Constants for Substituted Phenols in DMSO

Subst	ortho substituents		meta substituents			para substituents			
	δ, ppm	$\Delta\delta_o$	δ, ppm	$\Delta\delta_m$	$\sigma_m{}^a$	δ, ppm	$\Delta\delta_p$	$\sigma_p{}^a$	$\sigma^-{}^a$
H	9.23	0.00	...	...	0.00	...	...	0.00	
F	9.70	0.47				9.33	0.10	0.06	
Cl	10.00	0.77	9.81	0.58	0.37	9.60	0.37	0.23	
Br	10.07	0.84				9.62	0.39	0.23	
I	10.20	0.97				9.60	0.37	0.18	
NO$_2$	10.8	1.6	10.37	1.14	0.71	10.9	1.7	0.78	1.27
CN	10.97	1.74				10.55	1.32	0.66	0.90
CF$_3$	10.44	1.21	10.04	0.81	0.43	10.23	1.00	0.54	
CH$_3$	9.10	−0.13	9.15	−0.08	−0.07	9.03	−0.20	−0.17	
Et	9.07	−0.16				9.00	−0.23	−0.15	
n-Pr	9.06	−0.17				9.00	−0.23	−0.126^c	
i-Pr	9.07	−0.16				9.00	−0.23	−0.151	
sec-Bu	9.03	−0.20				9.00	−0.23	−0.123^c	
t-Bu	9.17	−0.06				9.03	−0.20	−0.197	
n-Pen						9.01	−0.22		
t-Pen	9.08	−0.15				9.00	−0.20	−0.190^c	
C$_6$H$_{11}$	9.05	−0.18				8.99	−0.24		
CH$_2$CH=CH$_2$	9.19	−0.04				9.03	−0.20		
CH=CHCO$_2$Me	10.17	0.94				10.00	0.77		
CH$_2$Ph	9.29	0.06				9.12	−0.11		
CH$_2$OH	9.18	−0.05							
Ph	9.46	0.23				9.55	0.32	−0.01	
CHO	10.75	1.52				10.57	1.34	0.22	1.13
COMe	11.97	2.74				10.28	1.05	0.50	0.87
COPh	10.61	1.38				10.43	1.20	0.459^c	
CO$_2$Me	10.55	1.32				10.24	1.01	0.436^b	0.636^b
CO$_2$CH$_2$Ph	10.51	1.28				10.31	1.08		0.667^c
OCOPh			9.74	0.51	0.33^d				
CONHPh	10.41	1.18							
OH	8.70	−0.53				8.55	−0.68	−0.37	
OMe	8.76	−0.47				8.80	−0.43	−0.27	−0.2
OEt	8.66	−0.37				8.81	−0.42	−0.24	
OPh			9.54	0.31	0.25	9.31	0.08	−0.32	
NHCOMe	9.29	0.06				9.04	−0.19	0.00	
NH$_2$	...^{e}	...	8.77	−0.46	−0.14	...^{e,f}	...		
NMe$_2$	8.78	−0.45				8.51	−0.72	−0.83	
SMe	9.59	0.36				9.36	0.13	0.00	
SOMe	10.50	1.37				10.00	0.77	0.49	
SO$_2$Me						10.49	1.26	0.72	1.05
NO						...^{e,g}	...		

^{a} From C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964), unless otherwise designated. ^{b} V. Pal'm, *Russ. Chem. Rev.*, **9**, 471 (1961). ^{c} H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). ^{d} J. G. Traynham and G. A. Knesel, *J. Org. Chem.*, **31**, 3350 (1966). ^{e} No hydroxyl absorption was observed. ^{f} The hydroxyl absorption for p-aminophenol in DMSO has been reported to be at δ 8.28 ($\Delta\delta$ = −0.94): R. J. Ouellette, *Can. J. Chem.*, **43**, 707 (1965). ^{g} p-Nitrosophenol exists in the tautomeric quinoid form in DMSO: R. K. Norris and S. Sternhell, *Australian J. Chem.*, **19**, 841 (1966).
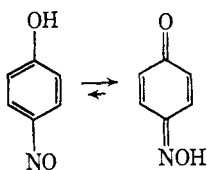
because of the greater number of substituent constants available, σ^- was selected as the most suitable description of the data (r = 0.967, s = 0.132, n = 30). The least-squares computed equation for the latter correlation is as follows

$$\sigma_p{}^- = 0.720\Delta\delta_p - 0.038 \qquad (2)$$

Six meta-substituted phenols were similarly studied. No correlation was found with the spectral data and σ_R, $\sigma_R{}^0$, or $\sigma_R{}^-$, and a poor correlation was found with σ_I (r = 0.899, s = 0.113, n = 7). However, the correlation between the Hammett σ_m values and $\Delta\delta_m$ is excellent (r = 0.984, s = 0.051, n = 7). The following equation for meta substituents was obtained.

$$\sigma_m = 0.547\Delta\delta_m + 0.043 \qquad (3)$$

When data for both meta- and para-substituted phenols are combined to form one set of data, an equally good correlation is observed between the σ^- and $\Delta\delta$ values (r = 0.965, s = 0.128, n = 36). The following equation was obtained.[18a,b]

$$\sigma_{m,p} = 0.700\Delta\delta_{m,p} - 0.029 \qquad (4)$$

This correlation is plotted in Figure 1 (ρ = 1.42).[18c]

(18) (a) To be compared with equations calculated by us from other data in the literature[9a,b] for phenols in DMSO
ref 9a (r = 0.989, s = 0.065, n = 14) (with correct σ = −0.303 for 3,4-dimethyl[9a])

$$\sigma^-{}_{m,p} = 0.650\Delta\delta_{m,p} + 0.019 \qquad (a)$$

ref 9b (r = 0.997, s = 0.031, n = 22)

$$\sigma^-{}_{m,p} = 0.710\Delta\delta_{m,p} - 0.009 \qquad (b)$$

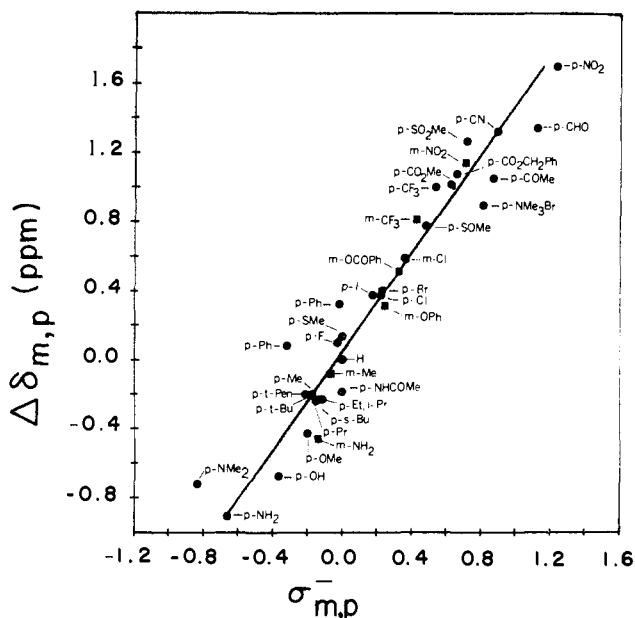(b) A difference in temperature [28[9a] and 40° (this work)] may ac-

Figure 1. Correlation of $\sigma^-_{m,p}$ with the relative hydroxyl chemical shifts from *meta-* and *para*-substituted phenols in DMSO. The equation for this linear relationship is $\sigma^-_{m,p} = 0.700\Delta\delta_{m,p} - 0.029$ ($r = 0.965$, $s = 0.128$, $n = 36$).
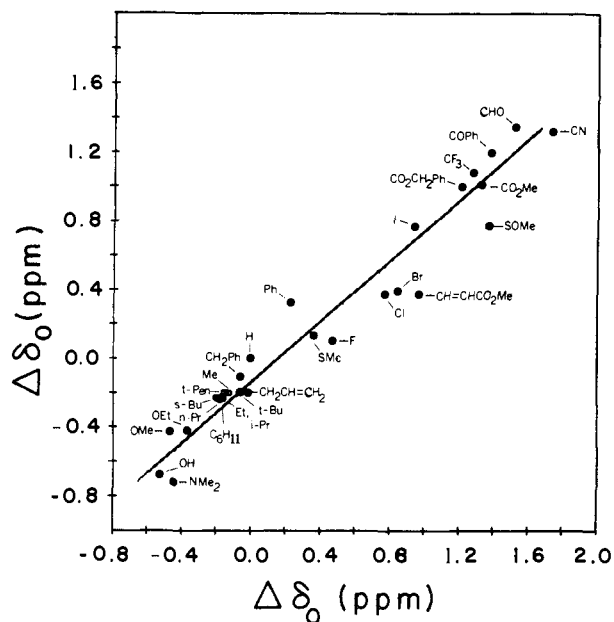

Figure 2. Correlation between the relative hydroxyl chemical shifts from *ortho-* and *para*-substituted phenols in DMSO. The equation for this linear relationship is $\Delta\delta_o = 1.13\Delta\delta_p + 0.161$ ($r = 0.975$, $s = 0.159$, $n = 29$).

Equations 2 and 3 imply that ρ_m and ρ_p are not actually the same, but differ slightly in this system. This difference is approximately 0.2ρ unit, which is not significant enough to warrant the use of separate ρ values in the correlation of *meta* and *para* chemical shifts. However, from a theoretical point of view, these data *do* seem to confirm Hine's[19] analysis that $\rho_m \neq \rho_p$ and are consistent with the similar conclusions of Jaffé.[20]

In an earlier paper,[9a] new σ constants were proposed for the m-OCOC₆H₅ and p-OSO₂C₆H₄CH₃-p groups from the hydroxyl chemical shifts of the substituted phenols in DMSO at 28°. From the data in Table I and the statistical correlation with σ_p^- (eq 2), we propose five new *para*-substituent constants listed in Table II.

Table II

Substituent	σ_p^-
p-C₆H₁₁	-0.20
p-(CH₂)₄CH₃	-0.19
p-CH₂CH=CH₂	-0.18
p-CH₂C₆H₅	-0.12
p-CH=CHCO₂CH₃	$+0.50$

From the observations that $\Delta\delta_m$ correlates with σ_m and not with σ_1, and σ_p^- is required in the correlation of $\Delta\delta_p$ values, it is evident that both inductive and reso-

count for the slight differences in chemical shifts reported in ref 9a and by us, but no rationalization is apparent for the differences reported in ref 9b and by us. Despite these differences, all three sets of data clearly reveal that σ^- is $\sim 0.7\Delta\delta$.

(c) To be compared with $\rho = 1.52$ calculated by us from data in ref 12. Although these authors[12] state that their use of σ^- rather than σ did not improve the correlation with $\Delta\delta$(HMPA), we find some improvement: σ^{-3c} leads to $r = 0.963$ ($s = 0.127$, $n = 23$) and σ^{15} to $r = 0.930$ ($s = 0.127$, $n = 23$). The equation calculated is

$$\sigma^-_{m,p} = 0.657\Delta\delta_{m,p} + 0.020 \qquad (c)$$

(19) J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959).
(20) H. H. Jaffé, *ibid.*, **81**, 3020 (1959).

nance factors influence the position of the hydroxyl absorption of substituted phenols in DMSO. For this reason, we suggest that this system allows a spectroscopic measurement to be made which is closely related to actual reactivity measurements, in contrast to the measurement of the ¹⁹F shielding parameters from substituted fluorobenzenes[21] which correlate with the inductive substituent constant, σ_1, alone.[22]

II. $\Delta\Delta$ ortho vs. $\Delta\Delta$ para

Branch and Calvin[4b] have discussed in detail the effects of *ortho* substitution upon reactivities of many benzene derivatives. In one instance these authors have shown through a plot of the dissociation constants of one set of *ortho*-substituted acids (*e.g.*, phenylboronic acids) vs. the dissociation constants of another set of similarly substituted acids (*e.g.*, benzoic acids), that an *ortho* effect may be demonstrated by deviations from linearity in this graph. That is, the presence of such effects may be demonstrated, but not the magnitude or direction of the effects. As McDaniel and Brown[23] have pointed out, "Only in the event that a reference system could be found free from *ortho* effects would it be possible to utilize such plots for the estimation of the magnitude and direction of *ortho* interactions." We believe that we have found such a system. This suggestion is supported by the excellent *linear* relation between $\Delta\delta_o$ and $\Delta\delta_p$ for 29 pairs of *ortho-* and *para*-substituted phenols in DMSO. The equation expressing this correlation follows ($r = 0.975$, $s = 0.159$, $n = 29$)[24]

(21) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *ibid.*, **74**, 4809 (1952).
(22) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709 (1963).
(23) D. H. McDaniel and H. C. Brown, *ibid.*, **77**, 3756 (1955).
(24) The o-NO₂ and o-COCH₃ substituents appear to interact with the phenolic hydroxyl intramolecularly in DMSO (*vide infra*); therefore, these groups are not used in any considerations of *ortho*-substituted compounds unless specifically designated.

and is plotted in Figure 2. The observation of parallel

$$\Delta\delta_o = 1.13\Delta\delta_p + 0.16 \qquad (5)$$

ortho and *para* spectral parameters is unusual and important. Hammett,[25] Taft,[26] and others have previously commented on expectations of parallel reactivity measurements for *ortho-* and *para*-substituted benzene derivatives.

The fact that the hydroxyl absorptions of *ortho-* and *para*-substituted phenols in DMSO are correlated in a linear manner indicates a proportionality between the interactions influencing the strength of the intermolecular OH···DMSO hydrogen bond in the isomeric phenols. We believe that the source of these parallel effects is most likely from electronic influences alone, acting in the absence of primary proximity interactions such as steric effects.[27]

This freedom from *ortho* effects can be ascribed to two effects: (1) the bulk of the DMSO···HO moiety orients itself away from the *ortho* substituent, and (2) the resonance-stabilized barrier to rotation about the C–O bond keeps the solvated hydroxyl from freely turning toward the *ortho* substituent.

Since random scatter is usually observed upon comparing the effects from *ortho* and *para* substituents, the high correlation ($r = 0.974$) of $\Delta\delta_o$ with $\Delta\delta_p$ offers a unique opportunity for analyzing in detail the electronic effects from *ortho* substituents—a problem which has long been considered insoluble.

A comparison of the $\Delta\delta_o$ and $\Delta\delta_p$ values for the substituents listed in Table I leads to the recognition of two extreme deviations (o-NO$_2$ and o-COCH$_3$) which should be omitted from all considerations involving $\Delta\delta_o$ values.

o-Nitrophenol exhibits a broad hydroxyl band at δ 10.8 which disappears from the nmr spectrum in less than 1 min, presumably *via* fast exchange of the hydroxyl proton with the solvent. The position of this absorption itself is broad (>20 Hz); the position of this absorption is much further upfield (in the direction of a *weaker* acid) than expected from the comparison with other $\Delta\delta_p$ values corresponding to strong electron-withdrawing substituents and from the results of other investigators.[12] This observation is presumably the result of partial intramolecular hydrogen bonding between the o-NO$_2$ group and the hydroxyl.[28]

o-Hydroxyacetophenone (o-acetylphenol), on the other hand, exhibits a sharp hydroxyl absorption, but at a δ value considerably further downfield than is commensurate with the relative acidity of the phenol. The position of the hydroxyl absorption in o-hydroxyacetophenone is not only completely out of the range of normal hydroxyl absorptions in DMSO, but is also only slightly dependent on solvent ($\delta_{\text{CCl}_4} = 12.03$,[29]

$\delta_{\text{DMSO}} = 11.97$). It is therefore apparent that the intramolecular hydrogen bond in this compound completely overcomes any tendency of the molecule to hydrogen bond to DMSO.[28,30]

The $\Delta\delta_o$ *vs.* $\Delta\delta_p$ plot (Figure 2) reveals that other carbonyl-containing substituents (such as CHO, COC$_6$H$_5$, CO$_2$CH$_2$C$_6$H$_5$, CO$_2$Me, and CONHC$_6$H$_5$) do not hydrogen bond intramolecularly to any effective degree with the OH in DMSO solutions. These data on the relative ability of o-acetyl to form a strong intramolecular hydrogen bond are consistent with the reports of other workers.[32] The competition of intra- *vs.* intermolecular hydrogen bonding in other hydrogen-bonding solvents may be of use as a probe to the strengths of intramolecular bonds in *ortho*-substituted phenols.[33]

From Figure 2 small deviations can also be seen: the o-SOCH$_3$ and o-CH=CHCO$_2$CH$_3$ substituents, for example, cause the hydroxyl absorption of the corresponding phenols to be further downfield than the correlation would normally suggest, and slight steric interference may be revealed by the relative upfield position for o-phenylphenol. These interpretations are made, of course, assuming that the deviations arise in the *ortho*-substituted phenol and not in the *para*-substituted one. The excellent fit of the data for o- and p-t-butylphenols is noteworthy.

With the exception of the methoxyl, ethoxyl, and phenyl groups, all *ortho* substituents are associated with δ values upfield from the *para* ones. In HMPA[12] even these *ortho*-substituted phenols exhibit hydroxyl absorptions at higher field than do the *para* isomers. Apparently in DMSO some interaction is occurring between the o-methoxyl, o-ethoxyl, and o-phenyl substituents and the hydroxyl, which is not completely overshadowed by the intermolecular hydrogen bond. Even these deviations are minor, however.

III. *ortho*-Substituent Constants

The study of *ortho*-substituted compounds and the concomitant quest for *ortho*-substituent constants relating the "true" electronic effects[34] of the substituent in the past have taken two distinct courses. First, the standard Hammett treatment is used with a system in which the reaction center is remote from the *ortho* substituent[35] or with one in which the transition state is otherwise free of steric and other proximity effects.[23,36]

(25) Reference 2, pp 206–207.

(26) Reference 3f, pp 586–597.

(27) This view is supported by the hydroxyl chemical shift values of 2,6-dimethylphenol ($\delta = 8.03$, $\Delta\delta = -1.20$) and 2,6-dimethoxyphenol ($\delta = 8.12$, $\Delta\delta = -1.11$). The sterically hindered hydroxyl in these compounds no longer reflects the effect of conjugation with the aromatic ring, and the $\Delta\delta$ values for these compounds indicate an increased shielding of the hydroxyl absorption completely out of the range suggested by additive effects from the two *ortho* substituents. In addition, the absorption for 2,6-dimethoxyphenol is *downfield* from that of 2,6-dimethylphenol, indicating that the methoxyl groups, like the hydroxyl, may be turned out of the plane of the ring and are electron withdrawing by inductive effect. For another interpretation of this phenomenon, see I. Yamaguchi, *Bull. Chem. Soc. Japan*, **34**, 451 (1961).

(28) I. Yamaguchi, *ibid.*, **34**, 353 (1961).

(29) S. Forsén and B. Åkermark, *Acta Chem. Scand.*, **17**, 1907 (1963).

(30) Since the intermolecular hydrogen bond between phenol and DMSO has an enthalpy of 6.5 kcal/mol at 30.7°[31] and an electron-withdrawing substituent normally enhances the strength of this hydrogen bond, the intramolecular hydrogen bond in o-hydroxyacetophenone must have a strength of at least 6.5 kcal/mol and is probably much stronger.

(31) R. S. Drago, B. Wayland, and R. L. Carlson, *J. Am. Chem. Soc.*, **85**, 3125 (1963).

(32) (a) I. M. Hunsberger, *ibid.*, **72**, 5626 (1950); (b) A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, *ibid.*, **82**, 5057 (1960); (c) N. M. Cullinane, R. A. Woolhouse, and V. V. Bailey-Wood, *Rec. Trav. Chim.*, **80**, 116 (1961).

(33) For example, the o-NO$_2$ and o-COCH$_3$ substituents show no evidence for intramolecular hydrogen bonding in HMPA.[12]

(34) For example, at the Second Conference on Linear Free Energy Relationships, University of California, Irvine, Calif., March 27–29, 1968, Professor F. G. Bordwell expressed an ambition to present a table of σ_T (σ "true") values.

(35) (a) P. Mamalis and H. N. Rydon, *J. Chem. Soc.*, 1049 (1955); (b) P. Mamalis and H. N. Rydon, *Nature*, **166**, 404 (1950); (c) M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955); (d) I. J. Solomon and R. Filler, *ibid.*, **85**, 3492 (1963); (e) J. D. Roberts and R. A. Carboni, *ibid.*, **77**, 5554 (1955).

(36) (a) N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1824 (1962); (b) P. D. Bolton, F. M. Hall, and I. H. Reece, *ibid., B*, 717 (1966); (c) F. J. Stubbs and C. Hinshelwood, *ibid.*, S71 (1949);

A number of ortho-σ constants calculated from various reaction or spectral measurements have been tabulated previously.[7a,36]

Reactivity measurements for ortho-substituted benzene derivatives more often than not reflect significant proximity interactions (even though attempts have been made in some cases to minimize these ortho effects) and result in widely scattered and inutile data points. The most widely accepted approach to the subject of ortho-substituent constants today is Taft's derivation of σ_o^* constants,[3f,37] even though there are troublesome assumptions in this approach with respect to the cancellation of steric and resonance effects in the ratio of rate constants from the acidic and basic hydrolyses of alkyl ortho-substituted benzoates.[3f] Because most investigators until now have had little faith in their ability to exclude all important steric effects from their reactivity or spectral measurements, σ_o^* values have remained the standard measure of ortho-polar effects. For this reason a comparison between the hydroxyl chemical shifts for ortho-substituted phenols in DMSO and the published σ_o^* constants was made. Only a moderately successful correlation was found between $\Delta\delta_o$ and these eight σ_o^* constants ($r = 0.934$, $s = 0.089$, $n = 8$).[24] We believe that the chemical shift measurements for ortho-substituted phenols in DMSO and HMPA represent a superior measure of electronic effects from ortho substituents. This conclusion is supported by the extremely precise correlation between the relative chemical shift data from ortho- and para-substituted phenols (vide infra) and by the precision of the correlations of the σ_o^- values (defined from chemical shift measurements) with reactivity data (Table IV).

A second approach involves the measurement and correlation of physical parameters of compounds likewise unencumbered with ortho interactions. The latter measurements have been mainly spectroscopic,[38] and in general have been the most successful in describing ortho-electronic effects in the absence of meaningful reactivity data. In many cases the geometry of the ortho-substituted benzene derivative can be altered through solvation or hydrogen-bonding influences so that observed parameters (such as change in absorption frequency or chemical shift) reflect no steric interactions. Usually spectroscopic methods have the additional advantage that the observed electronic effects originate only from the ground state or the transition state, and not a combination of both as commonly occurs in simple reactivity measurements. The convenience or manageability of spectroscopic measurements may be offset, of course, by their dissimilarity to reactivity measurements, and the ultimate test of any substituent constant lies in its ability to relate accurately the electronic influences of the substituent to the free

energy expression of interest. σ values obtained in this manner must in the end be related to reactivity data.

In DMSO the hydroxyl absorptions of ortho- and para-substituted phenols are correlated with each other in a linear manner. Absence of kinetic energy contributions due to steric interactions should allow a linear free energy expression to describe the electronic effects of ortho substituents in a manner analogous to the Hammett approach.[25]

From the equation of the line relating the relative chemical shift of para-substituted phenols to σ_p^- (eq 2), σ_o^- is defined. The calculated values of σ_o^- from this system are listed in column 1 of Table III. Included also in this table are σ_o^- values calculated from similar data for phenols in HMPA[12] and anilines in DMSO,[39] with the accompanying defining equations. When σ_o^- is defined in the above manner, the assumption is made that ρ is the same for both ortho and para substitution.[40] To our knowledge, Table III contains the most extensive tabulation of σ_o^- values available.

Table III. ortho-Substituent Constants

Substituent	σ_o^- a	σ_o^- b	σ_o^- c
H	0.00	0.00	0.00
F	0.29		
Cl	0.50		0.40
Br	0.55	0.66	0.40
I	0.64		
NO₂	...d	1.20	...d
CN	1.18		
CF₃	0.81		
Me	-0.13	-0.03	-0.17
Et	-0.15		
n-Pr	-0.16	-0.06	
i-Pr	-0.15	-0.03	
sec-Bu	-0.18	-0.07	
t-Bu	-0.08	0.00	
t-Pen	-0.15		
C₆H₁₁	-0.17	-0.08	
CH₂CH=CH₂	-0.07		
CH=CHCO₂Me	0.62		
CH₂Ph	-0.08		
CH₂OH	-0.07		
Ph	0.21	0.20	
CHO	1.02	0.92	
COMe	...d	1.06	
COPh	0.93		
CO₂Me	0.88		
CO₂CH₂Ph	0.86		
OCOMe	-0.01		
CONHPh	0.79		
OH	-0.41		
OMe	-0.37	-0.23	-0.20
OEt	-0.30		-0.23
NHCOMe	-0.08		
NMe₂	-0.36		
SMe	0.21		
SOMe	0.92		

a This work; phenols in DMSO: $\sigma_o^- = 0.720\Delta\delta_0 - 0.038$. b M. W. Dietrich, J. S. Nash, and R. E. Keller, Anal. Chem., 38, 1479 (1966); phenols in HMPA: $\sigma_o^- = 0.657\Delta\delta_0 + 0.020$. c B. M. Lynch, B. C. MacDonald, and J. G. Webb, Tetrahedron, 24, 3595 (1968); anilines in DMSO: $\sigma_o^- = 0.702\Delta\delta_0 - 0.023$. d Measurement unreliable.

(d) J. G. Mather and J. Shorter, J. Chem. Soc., 4744 (1961); (e) M. Charton, J. Am. Chem. Soc., 86, 2033 (1964); (f) C. L. Liotta, Second Conference on Linear Free Energy Relationships, University of California, Irvine, Calif., March 27-29, 1968; Chem. Commun., 338 (1968).

(37) For a brief but useful discussion of Taft's approach and uses of σ_o^* values, see J. F. Bunnett, in "Technique of Organic Chemistry," 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Volume VIII, Part I, Interscience Publishers, New York, N. Y., 1961, pp 226-229.

(38) (a) P. J. Bray and R. G. Barnes, J. Chem. Phys., 27, 551 (1957); (b) E. N. Tsvetkov, G. K. Semin, D. I. Lobanov, and M. I. Kabachnik, Tetrahedron Letters, 2521, 2933 (1967); (c) T. Yonemoto, W. F. Reynolds, H. M. Hutton, and T. Schaefer, Can. J. Chem., 43, 2668 (1965); (d) A. W. Baker and A. T. Shulgin, J. Am. Chem. Soc., 81, 1523 (1959).

(39) B. M. Lynch, B. C. MacDonald, and J. G. K. Webb, Tetrahedron, 24, 3595 (1968). We thank Dr. Lynch for sending a copy of his manuscript before publication (see ref 9a).

(40) Many investigators have often assumed that $\sigma_o = \sigma_p$ and $\rho_o = \rho_p$ for pragmatic reasons,[41] while still other investigators have found some experimental evidence for the latter equality.[42] In an apparently neglected theoretical paper, Hine[19] has shown that the completely general treatment of the Hammett equation requires different ρ for meta and
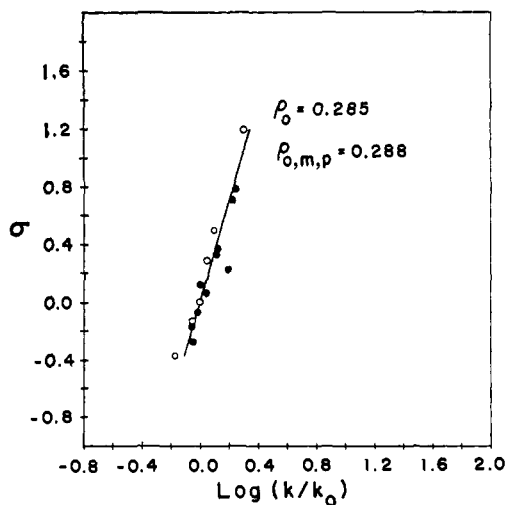
Figure 3. Hammett plot of the rate data from the pyrolysis of *ortho*-, *meta*-, and *para*-substituted isopropyl benzoates, 337.4° [G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, **28**, 3496 (1963); *ibid.*, **29**, 3533 (1964)]: O, *ortho* substituent; ●, *meta* or *para* substituent.
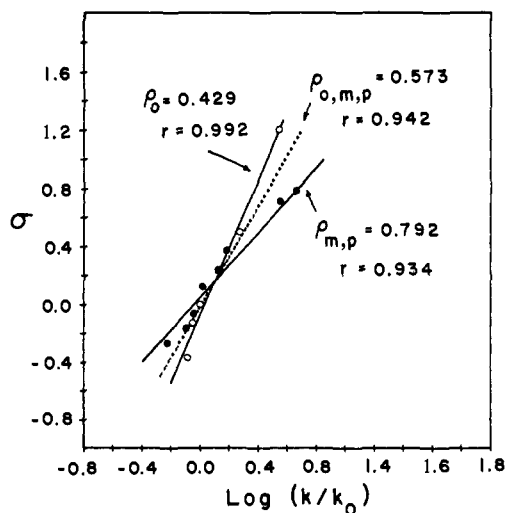

Figure 4. Hammett plot of the rate data from the alkaline fission of (*ortho*-, *meta*-, and *para*-substituted benzoyloxyethyl) dimethylsulfinium iodides, H_2O, 25° [P. Mamalis and H. Rydon, *J. Chem. Soc.*, 1049 (1955)]: O, *ortho* substituent; ●, *meta* or *para* substituent.

For these *ortho*-substituent constants to be meaningful, the application of them to observable reaction rates or equilibria is essential. Therefore, the values of σ_o^- listed in Table III were compared with literature data for *ortho*-substituted compounds. The standard Hammett approach (eq 1) was used in this comparison. In Table IV are listed the results of these comparisons for which the correlation coefficient was greater than 0.900. In spite of the surprising precision with which many of these data correlate with the *ortho*-substituent constants, it is difficult to tell at this time whether all the σ_o^- constants listed in Table III are accurate descriptions of the electronic effects, since in most cases the rate or equilibrium data for only a few *ortho*-substituted compounds are available for each reaction.[44]

A linear correlation between the *ortho*-substituent constant, σ_o^-, and log (k/k_0) for an individual reaction

para substitution, but seldom is the difference between ρ_m and ρ_p sufficient to be of major consequence.[19,21] The use of one ρ value for both *meta* and *para* substitution has resulted in successful correlations of thousands of reaction rate and equilibrium data, and we prefer also to accept the equality of ρ_o and ρ_p for purely pragmatic reasons. However, this approach does not prevent the reactivity correlations with σ_o^- from assuming a "pseudo-ρ_o" value quite different from ρ_p; in these cases the kinetic energy contributions from the *ortho* proximity interactions are proportional to the potential energy terms (described by the correlation of *meta*- and *para*-substituted compounds).[43]

(41) For example (a) J. Vene and J. Tirouflet, *Bull. Soc. Chim. France*, 220 (1954); (b) G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3238 (1955); (c) A. C. Farthing and B. Nam, in "Steric Effects in Conjugated Systems," G. C. Gray, Ed., Butterworth's Scientific Publications, London, 1958, p 131.

(42) (a) H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **76**, 1548 (1954); (b) J. D. Roberts and J. A. Yancey, *ibid.*, **73**, 1011 (1951); (c) K. U. Ingold, *Can. J. Chem.*, **38**, 1092, (1960).

(43) See, for example, Table IV, reaction 3 (Figure 4) and the accompanying discussion of this reaction.

(44) In these correlations with reactivity data, we use the value of 1.20 for the substituent constant for o-NO_2 (obtained from the data in ref 12). For comparison, the available Taft σ_o^* constants[37,45] were used for similar correlations of the same data. In each of these latter correlations, the appropriate σ_o^* constant for the o-NO_2 substituent was used ($\sigma_o^* = 0.78$ or $\sigma_o^* = 1.22$). This practice undoubtedly impairs the comparative status of our set of constants when no extended conjugation is apparent in the reaction under consideration; nevertheless, in most cases, these constants still produce correlations as good as or better than the σ^* constants do. An additional advantage to the use of σ_o^- constants is the larger tabulation of values available for further testing and utilization.

(45) Reference 3f, p 591. All σ_o^* values used in this reference are relative to H.

indicates that the σ constants for the substituents studied do accurately evaluate the electronic effects from the *ortho* substituent and that proximity effects are either absent, constant, or proportional to the electronic effects in the reactivity data. For example, for the pyrolysis of isopropyl 2-substituted benzoates[7a] (Table IV, reaction 1; Figure 3), an excellent correlation is found between the relative rate data and the σ_o^- constants when they are treated in the standard Hammett manner ($r = 0.989$, $\rho_o = 0.285$), the combined Hammett treatment of *ortho*-, *meta*-, and *para*-substituted compounds shows a somewhat poorer correlation, but one which has the same ρ value ($r = 0.942$, $\rho = 0.288$). No (or constant) *ortho* effects seem to be operable in this system. On the other hand, for the alkaline fission of (*ortho*-substituted benzoyloxyethyl)-dimethylsulfinium iodides[35a] (Table IV, reaction 3; Figure 4) the relative rate data from the *ortho*-substituted salts give an excellent correlation with σ_o^- ($r = 0.992$, $\rho_o = 0.429$), but the combined treatment for *ortho*-, *meta*-, and *para*-substituted compounds gives a poorer correlation with a different ρ value ($r = 0.942$, $\rho = 0.573$). The conclusion from this latter set of data is that the *ortho* effect in this system is a proportional factor, probably resulting from steric effects of the substituents with the alkyl side chain; resolution of the total linear free energy expression for *ortho*, *meta*, and *para* substituents for this reaction must then be described by a multiparameter equation exemplified in the type discussed by Taft[46] (eq 6), or by the use of a new *ortho* ρ value.[47]

$$\log (k/k_0) = \sigma\rho + \delta E_s \qquad (6)$$

It is our intention to investigate further the applicability of eq 6 and the utilization of separate ρ_o values

(46) Reference 3f, pp 597–603.

(47) The utilization of a new *ortho* ρ value or of eq 6 is based on the assumption that, in the defining measurement of *ortho*- and *para*-substituent effects (*i.e.*, the nmr spectra of substituted phenols in DMSO) $\rho_o = \rho_p$. We believe this assumption is justified in view of the precision of the correlations in Table IV.

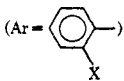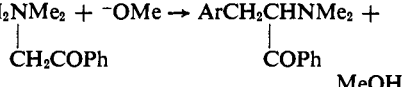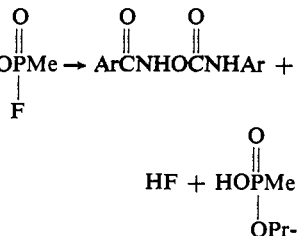**Table IV.** Correlation of σ_o^- with Reactivity and Spectral Data[a]

React. no.	Reaction $(Ar = \langle\bigcirc\rangle - X)$	Conditions	ρ^b	r^b	s^b	Substituents, X	Ref
1	ArCO₂Pr-i → ArCO₂H + CH₂=CHCH₃	337.4°	0.285 0.390*	0.989 0.991*	0.024 0.022*	H, OMe, Me, F, Cl, NO₂	c
2	ArCO₂Me + (Me)₃N → ArCO₂⁻ + Me₄N⁺	MeOH, 100°	0.997 0.969*	0.992 0.969*	0.074 0.154*	H, OMe, Cl, CO₂Me, NO₂ / H, OMe, Cl, NO₂	d
3	ArCO₂(CH₂)₂SMe₂I + OH⁻ → ArCO₂⁻ + CH₂=CHSMe₂I + H₂O	H₂O, 25°	0.429 0.578*	0.992 0.967*	0.033 0.068*	H, OMe, Me, Cl, NO₂	e
4	ArCH₂NMe₂ (CH₂COPh) + ⁻OMe → ArCH₂CHNMe₂ (COPh) + MeOH	MeOH, 16.4°	2.05 2.76*	0.962 0.903*	0.311 0.489*	H, OMe, Me, Cl, Br, I, NO₂	
5	ArCOH, pKₐ (NOH)	0.1 M KNO₃, 30°	0.495	0.985	0.064	H, NMe₂, OMe, NO₂	g
6	2ArCOH (NOH) + i-PrOPMe → ArCNHOCNHAr + HF + HOPMe (OPr-i)	H₂O, 30.5°	−0.377	0.295	0.115	H, NMe₂, OMe, NO₂	g
7	ArCH=CHCO₂H, pKₐ	H₂O, 25°	0.264 0.310*	0.943 0.905*	0.058 0.065*	H, OH, OMe, Me, Cl, NO₂ / H, OMe, Me, Cl, NO₂	h
8	ArOCH₂CO₂H, pKₐ	H₂O, 25°	0.276 0.379*	0.999 0.993*	0.005 0.021*	H, OMe, Me, Cl, NO₂	i, j
9	ArSCH₂CO₂H, pKₐ	H₂O, 25°	−0.257 0.370*	0.928 0.965*	0.064 0.045*	H, OMe, Me, Cl, NO₂	i, j
10	ArSeCH₂CO₂H, pKₐ	H₂O, 25°	0.238 0.320*	0.996 0.985	0.016 0.029*	OMe, Me, Cl, NO₂	i
11	ArC≡CCO₂H + MeOH →(H⁺) ArC≡CCO₂Me + H₂O	MeOH, 25°	−0.146 −0.204*	0.934 0.952*	0.038 0.033*	H, OMe, Cl, NO₂	k
		MeOH, 35°	−0.138 −0.196*	0.924 0.958*	0.039 0.029*	H, OMe, Cl, NO₂	k
12	ArC≡CCO₂H + Ph₂CN₂ → ArC≡CCO₂CHPh₂ + N₂	Dioxane, 30°	0.378 0.609*	0.953 0.968*	0.056 0.053*	H, F, CF₃, Cl, NO₂ / H, F, Cl, NO₂	l, m
13	ArC≡CCO₂H, pKₐ	35% dioxane, 25°	0.327 0.462*	0.972 0.956*	0.044 0.061*	H, OMe, F, Cl, CF₃, NO₂ / H, OMe, F, Cl, NO₂	k, m
14	ArCH₂CH₂CO₂H, pKₐ	H₂O, 25°	0.168 0.235*	0.932 0.943*	0.041 0.037*	H, OMe, Me, Cl, NO₂	h, n
15	ArNH₃⁺, pKₐ	H₂O, 25°	−2.70 −3.22*	0.946 0.962*	0.472 0.452*	H, OH, OMe, OEt, Me, t-Bu, Ph, F, Cl, Br, CO₂Me, NO₂ / H, OMe, OEt, Me, F, Cl, Br, NO₂	o
16	ArCH=N–(ring, H-O), ΔνOH	CCl₄	0.177 0.243*	0.992 0.996*	1.19 0.873*	H, OMe, Me, F, Cl, NO₂	p
17	ArOH, ΔδOH	DMSO, 28°	1.41 2.57*	0.967 0.964*	0.111 0.129*	H, Me, Ph, Cl, Br / H, Me, Cl, Br	q
18	ArNH₂, ΔδNH₂	DMSO	0.734 1.10*	0.986 0.933*	0.049 0.106*	H, OMe, OEt, Me, Cl, Br / (o-NO₂ omitted)	r
19	(pyridine) N, X, pKa	50% EtOH, 25°	−4.89	0.997	0.121	H, Me, Et, i-Pr, t-Bu, I	s
20	pyridine(N, X) + PhCO₃H → pyridine(N→O, X) + PhCO₂H	PhNO₂, 25°	−4.06 −7.46*	0.997 0.962*	0.115 0.386*	H, Me, Cl, Br	t
21	pyridine(N, X) + MeI → N⁺–Me I⁻ (X)	PhNO₂, 25°	−3.57 −6.18*	0.996 0.876*	0.329 0.614*	H, Me, Cl, Br	u

Table IV. *(Continued)*

React. no.	Reaction	Conditions	ρ^b	r^b	s^b	Substituents, X	Ref
22	ArCO₂H + CH₃CH(OH)₂ → ArCO₂⁻ + [CH₃CH(OH)(OH₂⁺)]	H₂O, 25°	0.554	0.989	0.052	H, OMe, Me, Cl, NO₂	v
			0.785*	0.973*	0.081*		
23	HO—⟨⟩—N₂Cl ⇌ O—⟨⟩—N₂ + HCl	Aqueous MeOH, 22°	−4.94	0.981	0.287	H, Me, i-Pr, t-Bu, Br	w
24	Me—⟨⟩—OH + I₂ → Me—⟨⟩—OH (I)	H₂O, 25°	−2.89	0.992	0.189	H, Me, Pr, i-Pr, allyl, Br, I, NO₂	x
		0.2 M KI	−2.57*	0.935*	0.526*	H Me, Br, I, NO₂	
25	ArOP(OEt)₂ + OH⁻ → ArO⁻ + HOP(OEt)₂	H₂O, 25°	1.30	0.963	0.196	H, NMe₂, OMe, Et, i-Pr, Br, Cl, I, NO₂	y
			1.58*	0.954*	0.191*	H, OMe, Br, Cl, I, NO₂	
26	ArNH₂, pKb	H₂O, 25°	2.66	0.956	0.478	H, OMe, OEt, Me, Cl, Br, CO₂Et, NO₂	z
			2.94*	0.954*	0.507*	H, OMe, OEt, Me, Cl, Br, NO₂	
27	ArNHNH₂, pKb	H₂O, 25°	1.09	0.940	0.228	H, OMe, OEt, Me, Cl, Br, CO₂Et, NO₂	z
			1.31*	0.979*	0.147*	H, OMe, OEt, Me, Cl, Br, NO₂	
28	ArCO₂H, pKₐ	50% DMSO	−0.104	0.983	0.011	H, OMe, i-Pr, Me, Cl, NO₂	aa
			−0.139*	0.956*	0.019*	H, OMe, Me, Cl, NO₂	
29	ArC=NOCN(H)(O)/(CH₃) + H₂O → ArC=NOH	0.1 M Na₃PO₄	0.756	0.955	0.083	H, OMe, OEt, i-Pr, t-Bu, SMe, Br	bb

ᵃ Some of these reactions have been previously tabulated by Charton: M. Charton, *Can. J. Chem.*, **38**, 2493 (1960); *J. Am. Chem. Soc.*, **86**, 2033 (1964). ᵇ The first line of correlation data for each reaction refers to comparisons with σ_o^- (this work); the second line (where applicable) refers to the comparisons with Taft's σ_o^* values and is denoted with an (*). ᶜ D. A. D. Jones and G. G. Smith, *J. Org. Chem.*, **29**, 3531 (1964). ᵈ L. P. Hammett and H. L. Pfluger, *J. Am. Chem. Soc.*, **55**, 4079 (1933). ᵉ P. Mamalis and H. N. Rydon, *J. Chem. Soc.*, 1049 (1955). ᶠ T. Thomson and T. S. Stevens, *ibid.*, **55** (1932). ᵍ M. A. Stolberg and W. A. Mosher, *J. Am. Chem. Soc.*, **79**, 2618 (1957). ʰ J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1426 (1937). ⁱ O. Behaghel, *J. Prakt. Chem.*, **114**, 287 (1926). ʲ O. Behaghel and M. Rollmann, *Chem. Ber.*, **62**, 2693 (1929). ᵏ M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955). ˡ J. D. Roberts and R. A. Carboni, *ibid.*, **77**, 5554 (1955). ᵐ I. J. Solomon and R. Filler, *ibid.*, **85**, 3492 (1963). ⁿ J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1008 (1937); J. F. J. Dippy and J. E. Page, *ibid.*, 357 (1938). ᵒ H. C. Brown, D. H. McDaniel, and O. Häfliger in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, p 592. ᵖ A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **81**, 1523 (1959). �q J. G. Traynham and G. A. Knesel, *J. Org. Chem.*, **31**, 3350 (1966). ʳ B. M. Lynch, B. C. MacDonald, and J. G. K. Webb, *Tetrahedron*, **24**, 3595 (1968). ˢ H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953); J. Holubek and J. Volke, *Collection Czech. Chem. Commun.*, **27**, 680 (1962). ᵗ A. Dondoni, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **91**, 613 (1961). ᵘ G. Coppens, F. Declerck, C. Gillet, and J. Nasielski, *Bull. Soc. Chim. Belges*, **72**, 25 (1963); A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948). ᵛ R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc.*, (London), A**197**, 141 (1949). ʷ G. A. Nikiforov, L. G. Plekhanova, and V. V. Ershov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 452 (1967); *Chem. Abstr.*, **67**, 32243f (1967). ˣ W. E. Mayberry, *Biochemistry*, **6**, 1320 (1967). ʸ C. van Hooidonk and L. Ginjaar, *Rec. Trav. Chim.*, **86**, 449 (1967). ᶻ H.-H. Stroh and G. Westphal, *Chem. Ber.*, **96**, 184 (1963). ᵃᵃ M. Hojo, M. Utaka, and Z. Yoshida, *Kogyo Kagaku Zasshi*, **69**, 885 (1966); *Chem. Abstr.*, **66**, 2121y (1967). ᵇᵇ R. L. Jones, private communication, Sept 3, 1968; data to be published in Ph.D. dissertation of R. L. J., University of California, Riverside, Calif.

in the description of reactivity data for *ortho*-substituted compounds which *do* incorporate *ortho* effects.

Finally, our concern about the make-up of the *ortho*-substituent effects has led us to infer that, because of the parallel effects of *ortho* and *para* substituents, the identity (but not necessarily the relative magnitudes) of the contributions to the substituent effects may be the same. We have chosen to investigate inductive and resonance contributions to σ_o^- in terms of the σ_I and σ_R^- parameters of Taft.[22,48] A computer-programmed computation based upon an iterative procedure pro-

duces the following equation,[49] which is illustrated in

$$\sigma_o^- = 1.29\sigma_I + 0.625\sigma_R^- \qquad (7)$$

Figure 5 ($r = 0.966$, $s = 0.126$, $n = 14$). Of course, other possibilities exist for describing the increase of *ortho*-electronic effects over those from the *para* position.

The closer proximity of the *ortho* substituent is undoubtedly responsible for the larger inductive contribution in the *ortho* position than in the *para* one; however, the reason for the decrease of resonance influences indicated by eq 7 is not at all evident.

(48) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).

(49) A three-parameter equation utilizing identical resonance effects for *ortho*- and *para*-substituent constants was unsuccessful in correlating σ_o^- values.
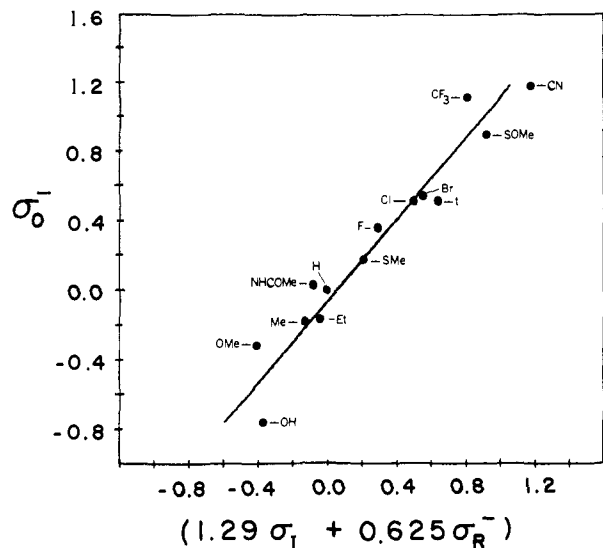
Experimental Section

Nmr data were obtained with a Varian Associates A-60A spectrometer equipped with a V-6040 variable-temperature controller. Dimethyl sulfoxide (Crown Zellerbach) was dried over barium oxide, distilled (10 mm) over calcium hydride, and stored over Linde Type 4A activated Molecular Sieve. All of the phenols used are well-characterized compounds. Most were acquired commercially, but some were synthesized according to descriptions in the literature.[50] Samples used met the usual melting point and/or gas chromatographic criteria for purity.

Phenol solutions were prepared in concentrations up to $\sim 10\%$ (w/v). The OH absorption was demonstrated to be independent of concentration for all phenols studied by a minimum of four separate runs of each compound at various concentrations at a constant temperature of $40 \pm 1°$. The chemical shifts of all phenols investigated were found to be temperature dependent, and extreme care was exercised to equilibrate every sample in the nmr spectrometer before the hydroxyl chemical shift was recorded. All resonances are reported in parts per million (ppm) downfield from the internal standard, tetramethylsilane.

Dual parameter statistical analysis was performed with a linear least-squares program on an IBM 7040 computer. All correlations of this type were plotted on a Calcomp 563 incremental plotter coupled to a Calcomp 570 magnetic tape unit. Multiple parameter analysis was performed with a linear iterative least-squares program (Louisiana State University Computer Center code: NLLSCF).

(50) The Ph.D. dissertation of M. T. T. may be consulted for detail
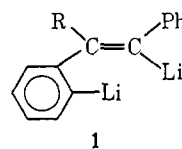
Organolithium Compounds and Acetylenes. V. Electron Transfer Plus Addition–Metalation in the Case of a Tertiary Organolithium Compound[1]

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Abstract: The reaction of *t*-butyllithium with diphenylacetylene at 70° results in products arising from electron transfer, *cis,cis*-1,2,3,4-tetraphenylbutadiene and *trans*-stilbene. At lower temperature, products arising from addition and metalation are obtained, namely 7, 8, and 9. Factors affecting the kinds of products and their stereochemistry are discussed.

W e have previously reported[4] that primary organolithium compounds react with diphenylacetylene (DPA) in ethyl ether to give a product resulting from *o*-metalation as well as addition to the triple bond. The dilithiated product was shown to have the *trans* configuration and may be stoichiometrically represented as 1, although the degree of association or dissociation to ions or ion pairs is not known.[5]

(1) (a) Research supported by AFOSR(SRC)-OAR, USAF Grant No. 720-65. (b) For paper IV, see J. E. Mulvaney and L. J. Carr, *J. Org. Chem.*, **33**, 3286 (1968).

(2) (a) Postdoctoral fellow supported by the University of Arizona "Science Development Program." (b) NASA Predoctoral Fellow, 1964–1966.

(3) Socony Mobil Predoctoral Fellow, 1962–1964.

(4) (a) J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963); (b) J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlung, and D. J. Newton, *ibid.*, **88**, 476 (1966).

(5) For a report concerning intramolecular addition of organolithium compounds to acetylenes, see S. A. Kandil and R. E. Dessy, *ibid.*, **88**, 3027 (1966).

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In contrast, either primary or tertiary organolithium compounds react with an alkylphenylacetylene such as methylphenylacetylene by abstracting protons to produce polylithiated species.[1b]

We report here reactions of DPA with *t*-butyllithium, a system in which either addition–metalation or reductive dimerization may occur.

Results and Discussion

Reactions of *t*-butyllithium with DPA were carried out in ligroin. That reaction occurred at all is a manifestation of the greater reactivity of the tertiary