acids in 50% butyl Cellosolve[8] and of substituted 1-naphthylamines in water.[9] These values are compared with ours in the following paper.

Experimental

Materials.—The acids and esters described in part II were stored overnight in a vacuum desiccator before use. Sodium hydroxide (0.05 *N*) was prepared by dilution of stock solutions supplied by B.D.H. Ltd. Carbon dioxide-free water was used and the solution changed weekly.

Water was demineralized and degassed by pumping off carbon dioxide under vacuum for one hour. Ethanol was dried over lime and fractionated off lime using a 61-cm. column packed with Dixon nickel gauzes. The middle fraction, b.p. 78°, was collected.[10]

Method.—Samples of the acids, sufficient to give 0.002 *M* solutions, were weighed into stoppered tubes. The acids were dissolved in ethanol (25 ml.) (warming was occasionally necessary), and diluted with water (25 ml.). Grade "A" pipets were used. These solutions were exactly half neutralized with the calculated quantity of aqueous (0.05 *N*) sodium hydroxide delivered from a calibrated 2-ml. side-arm buret. An equal volume of ethanol was added from a similar buret. The contents of the burets and their reservoirs were protected from atmospheric carbon dioxide by soda-lime guard tubes. The tubes containing the half neutralized solutions were thermostated at 25 ± 0.1° for 1 hour in an oil-bath. The e.m.f.'s of these solutions were measured with a Doran Universal *p*H meter with a glass electrode and saturated potassium chloride–calomel reference electrode. The e.m.f.'s expressed in *p*H units were read directly from the instrument.

Six different acids were measured at a time, one of them always being 1-naphthoic which served as a check on the behavior of the electrodes and meter. Benzoic acid was also measured as an additional check. Before and after measuring each batch of six acids the *p*H meter was checked by measurements on standard buffers at *p*H 4.00 and 5.60. If changes larger than *p*H 0.01 were observed the previous measurements were ignored. Care was taken to ensure that all solutions in which the electrodes were stored or washed and all standards were kept at 25 ± 0.1° in the oil thermostat. The buffers used for standardizations were a 0.05 *M* potassium hydrogen phthalate solution of *p*H 4.005 at 25° (British Standard 1647, 1950 *p*H scales), and a *p*H 5.60 buffer made up to the Clark and Lub formula and electrochemically standardized, by the suppliers, against a *p*H 4.000 buffer.

For the infrared measurements solutions of the substituted methyl naphthoates were prepared in dry chloroform in concentrations of about 0.7%. The infrared spectra of the carbonyl peaks were located between 5–6 μ. This region was scanned at 1μ/8 min. using a Grubb Parsons GS2A grating spectrometer. The measured resolution of this instrument was ±0.5 cm.$^{-1}$.

P.J.G. gratefully acknowledges the award of a maintenance grant by the Department of Scientific and Industrial Research. We wish to thank Mr. P. D. Cook for determining the infrared spectra.

(8) E. Berliner and E. H. Winicov, *J. Am. Chem. Soc.*, **81**, 1630 (1959).

(9) A. Bryson, *ibid.*, **82**, 4862 (1960).

(10) A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, *Technique of Organic Chemistry*, **8**, 339 (1955).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Substituent Effects. IV.[1] A Quantitative Theory

BY MICHAEL J. S. DEWAR AND PATRICK J. GRISDALE

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Analysis of the data presented in part III[1] suggests that the propagation of inductive effects by the successive polarization of σ-bonds (σ-inductive effect) is unimportant. The "inductive effect" of organic chemists is in reality a field effect. A general theory of substituent effects is developed on this basis, the σ-constants of a given substituent being expressed in terms of two parameters which are calculated from data for benzene. The theory is applied successfully to data for naphthalene and biphenyl and possible future developments of it are outlined.

The possible modes of action of substituents and their variation with the distance between the substituent and a reaction center were discussed in part I[2]. There are at least five different mechanisms by which the effects of a substituent can be transmitted through a conjugated molecule and it is as yet impossible to estimate their relative importance theoretically. The new data presented in the preceding paper[1] seem to lead to definite conclusions concerning this.

Three modes of transmission involve the primary inductive effects of substituents (the field, σ-inductive and π-inductive effects) while two depend on resonance interactions (mesomeric and electromeric effects). The last of these is unimportant except when there is mutual conjugation[3] between the substituent and the reaction center; we shall assume that substituents do not affect the properties of aromatic carboxylic acids in this way. (This assumption underlies the standard definition of Hammett σ-constants; it is probably a good approximation except possibly for powerful −E substituents such as NH_2.[4])

Jaffé[5] has assumed that the first two effects (field and σ-inductive) are also unimportant; he supposed that substituents in aromatic systems act only by polarizing the π-electrons, the σ-constant being proportional to the net formal charge at the point of attachment of the reaction center. He calculated this charge, produced by the π-inductive and mesomeric effects of substituents, using a simple MO treatment. As we have seen in part I,[2] the underlying assumptions are almost certainly incorrect; for the effects of substituents in saturated systems are very similar to their effects in aromatic systems. The field and/or σ-inductive effects must therefore be comparable with the other two. In confirmation we have compared the charge densities in the 1-position of naphthalene calculated for various substituents by Jaffé's method, with the σ-constants reported

(1) Part III, *J. Am. Chem. Soc.*, **84**, 3546 (1962). This work was carried out under Army Ordnance Research Contract No. DA-11-022-ORD-3451.

(2) M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539 (1962).

(3) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3351 (1952), theorems 47–49.

(4) *Cf.* H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

(5) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 778 (1952); *J. Am. Chem. Soc.*, **76**, 4261, 5843 (1954); **77**, 274 (1955).

in part III.[1] As Fig. 1 shows there is no correlation between the two quantities. The discrepancies are too great to be ascribed to the use of a simple and very approximate MO treatment; they must imply that some important effect is operating other than those considered by Jaffé. (The values for the charge densities were communicated to us by Dr. L. C. Snyder, Bell Telephone Laboratories, who calculated them using an IBM 704 computer.)

This alternative mode of transmission might involve either a σ-inductive effect or a field effect: the majority of organic chemists seem to have favored the former alternative. Here the transmission is supposed to take place by successive polarization of the carbon–carbon σ-bonds separating the substituent from the reaction center, the polarization decreasing in the ratio ϵ:1 in passing from one bond to the next. Branch and Calvin[6] and McGowan[7] have analyzed the effects of substituents on the strengths of acids and bases in this way and have concluded the transmission factor, ϵ, must have a value in the range 0.35–0.50.

Now the results reported in our previous paper[1] cannot be explained in terms of a σ-inductive effect unless ϵ is considerably greater than 0.50. This can be seen very clearly from the values listed in Table I for the σ-constants of substituents in the 3- and 6-positions of 1-naphthoic acid. Since resonance interactions between the 1,3- and 1,6-positions must be small, the effects of the substituents must be essentially inductive; if the mode of transmission is a σ-inductive effect, our results require $\epsilon \sim 0.65$, a value inconsistent with the data for saturated systems. Similar conclusions can be drawn from the σ-constants reported by Berliner and Blommers[8] for substituents in the 3′-position of biphenyl-4-carboxylic acid where resonance interactions must again be negligible (Table I).

It can moreover be shown that ϵ cannot possibly be as large as 0.35, the minimum value needed to explain the effects of substituents in saturated systems; for if it were, the increase in dipole moment with increasing chain length in a series of homologous normal alkyl derivatives of the type $CH_3(CH_2)_nX$ would be greater than that observed. From the data for alkyl halides one can estimate in this way that ϵ cannot be greater than 0.2. It is interesting that the majority of quantum chemists have used a still smaller value for ϵ in their calculations, usually about one-eighth.[9]

TABLE I

COMPARISON OF σ-CONSTANTS IN NAPHTHALENE AND BIPHENYL WITH DERIVED VALUES FOR THE INDUCTIVE TRANSMISSION PARAMETER

Compound	Substituent	i	j	σ_{ij}	ϵ
Naphthalene	O_2N	3	1	0.61	0.71
	O_2N	6	1	.41	
	NC	3	1	.59	.64
	NC	6	1	.34	
	Br	3	1	.34	.59
	Br	6	1	.18	
Biphenyl	O_2N	3	4	.71[a]	.64
	O_2N	3'	4	.23	
	Br	3	4	.26[a]	.70
	Br	3'	4	.12	

[a] Assumed equal to σ_m in benzene. This assumption is justified by the fact that substituent effects in benzene are usually additive; any effect of steric inhibition of coplanarity would be small here since a phenyl substituent cannot produce charges by a mesomeric effect.

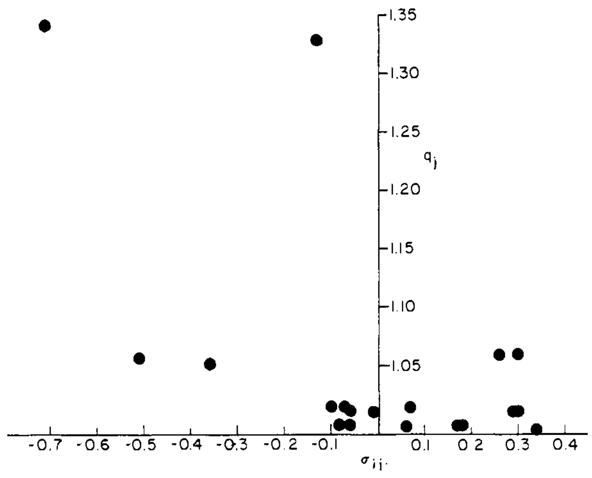

Fig. 1.—Plot of the calculated π-electron density at the 1-position for various monosubstituted naphthalene against the σ-constants deduced[1] from the pK's of the corresponding 1-naphthoic acids.

These arguments suggest that the so-called "inductive" effect of organic chemists may in fact be a field effect and that propagation by successive polarization of σ-bonds (*i.e.*, the σ-inductive effect) may be unimportant at positions separated from a substituent by more than one or two bonds. This would not be a very surprising conclusion. The importance of the field effect cannot be doubted in view of the classic work of Kirkwood and Westheimer[10] on the dissociation constants of dibasic acids, whereas there is no direct evidence that the σ-inductive effect can be propagated through more than one bond. On the contrary, several lines of evidence suggest that the attenuation factor (ϵ) is small. Thus the fact that *m*-aminophenyltrimethylammonium chloride is a weaker base than the *p*-isomer indicates[11] that the trimethylammonium group does not exert a significant π-inductive effect; and this in turn shows that there can be no appreciable change in the electronegativity of the adjacent carbon atom in the ring. Even a whole unit of positive charge on a nitrogen atom apparently fails to produce any significant polarization of adjacent N–C bonds.

For reasons indicated in part I[2] we may assume that the field effect of a substituent attached at atom i on a side-chain attached at atom j is given approximately by F/r_{ij}, F being a measure of the

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(6) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1941.

(7) J. C. McGowan, *Nature*, **159**, 644 (1947); *Chemistry & Industry*, 632 (1948).

(8) E. Berliner and E. A. Blommers, *J. Am. Chem. Soc.*, **73**, 2481 (1951); **82**, 6427 (1960).

(9) *E.g.*, H. C. Longuet-Higgins and C. A. Coulson, *J. Chem. Soc.*, 971 (1949).

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

(11) J. D. Roberts, R. A. Clement and J. J. Drysdale, *J. Am. Chem. Soc.*, **73**, 2181 (1951).

field set up by the substituent and r_{ij} the distance between atoms i and j. Since we are assuming the σ-inductive effect to be unimportant, and also limiting ourselves to cases where there is no mutual conjugation between the substituent and the reaction center, the only other factors to be considered are the π-inductive and mesomeric effects. These two effects vary in approximately the same way with the orientation of a given substituent,[2] the net effect being given[2] approximately by one of the expressions

$$Mq_{ij} \text{ or } -M'\pi_{ij} \qquad (1)$$

where π_{ij} is the atom–atom polarizability of atoms i and j, q_{ij} is the formal charge at position j produced by attaching the group $-CH_2^-$ at position i, and M or M' is a measure of the combined π-inductive–mesomeric effect of the substituent. The over-all σ-constant is then given by

$$\sigma_{ij} = F/r_{ij} + Mq_{ij} \qquad (2)$$

or

$$\sigma_{ij} = F'/r_{ij} - M'\pi_{ij} \qquad (3)$$

The signs in eq. 2 and 3 are chosen so that M, M' for a given substituent should have similar signs. The constants F, M or F', M' can be found for a given substituent from σ_m and σ_p for benzene, and σ-constants for any other system can then be calculated from eq. 2 or 3. Note that r_{ij} is the distance between the atoms in the ring to which the substituent and the reaction center are attached, expressed in terms of the C–C bond length in benzene. The quantities q_{ij} can be calculated very easily by the method of Longuet-Higgins,[12] who tabulated values for a number of systems. Atom–atom polarizabilities are somewhat troublesome to calculate, but values for all the common ring systems are listed in a recent compilation.[13]

Table II shows the values used in this paper. As our calculation of the field effect is in any case very approximate, we assumed for simplicity that all C–C bonds had the same length as those in benzene.

Table II

Values of r_{ij}, π_{ij} and q_{ij} for Various Hydrocarbons

Compound	i	j	r_{ij}	π_{ij}	q_{ij}
Benzene	1	3	$\sqrt{3}$	0.009	0
	1	4	2	− .102	1/7
Naphthalene	1	3	$\sqrt{3}$	.018	0
	1	4	2	− .139	1/5
	1	5	$\sqrt{7}$	− .023	1/20
	1	6	3	.007	0
	1	7	$\sqrt{7}$	− .033	1/20
Biphenyl	4	3'	$\sqrt{21}$	.....	0
	4	4'	5	.....	1/31

Table III lists values of F, M, F', M', calculated from the σ-constants compiled by McDaniel and Brown.[14]

Table IV compares the σ-constants calculated from eq. 2 and 3 for a variety of substituents in naphthalene, the reaction center being in the 1-position; the cases chosen are those for which experimental data are available[1] for comparison. The values from eq. 3 are given in parentheses. It will be seen that the two prime equations give very similar results.

Table III

Values for F, M, F', M' Calculated from σ_m and σ_p in Benzene

Substituent	F	M	F'	M'
Me	−0.12	−0.77	−0.14	−1.00
Et	− .12	− .64	− .13	−0.83
t-Bu	− .17	− .78	− .19	−1.02
Ph	.10	− .42	− .11	−0.55
F_3C	.74	1.12	0.77	1.46
NC	.97	1.23	1.00	1.60
CH_3CO	.65	1.24	0.68	1.62
EtOOC	.64	0.91	.66	1.19
HOOC	.64	.91	.66	1.19
^-O_2C	− .17	.60	− .15	0.78
Me_3SiCH_2	− .28	−1.37	− .32	−1.78
Me_3Si	− .07	−0.25	− .08	−0.33
H_2N	− .28	−3.64	− .38	−4.75
CH_3CONH	.36	−1.26	− .33	−1.64
Me_3N^+	1.52	0.39	1.53	0.51
O_2N	1.23	1.14	1.26	1.48
HO_3P	0.35	0.60	0.37	0.78
MeO	.20	−2.58	.13	−3.36
EtO	.17	−2.28	.11	−2.97
N-PrO	.17	−2.35	.11	−3.06
i-PrO	.17	−3.75	.07	−4.89
n-BuO	.17	−2.84	.10	−3.70
n-AmO	.17	−3.01	.09	−3.92
PhO	.44	−3.78	.34	−4.92
HO	.21	−3.36	.12	−4.38
CH_3COO	.68	−4.55	.56	−5.93
MeS	.26	−0.91	.24	−1.19
HS	.43	− .49	.42	−0.64
CH_3COS	.68	.70	.70	.91
CH_3SO	.90	.28	.97	.37
CH_3SO_2	1.04	1.40	1.08	1.83
H_2NSO_2	0.80	1.19	0.83	1.55
Me_2S^+	1.73	0.20	1.74	0.25
O_3S^-	0.09	.28	0.10	.37
MeSe	.17	− .56	.16	− .73
F	.58	−1.61	.56	−2.10
Cl	.65	−0.70	.63	−0.91
Br	.68	− .77	.66	−1.00
I	.61	− .84	.59	−1.10
IO_2	1.21	1.05	1.24	1.37

Figure 2 shows a plot of the σ-constants calculated from eq. 2 (*FM* method) with those measured experimentally.[1] All the points lie close to the theoretical line of unit slope, the standard deviation being 0.083 σ-unit. The constants calculated from eq. 3 (*F'M'* treatment) fit slightly better (standard deviation 0.075 σ-unit), but the difference is very small. The *FM* treatment has the advantage of greater simplicity, the quantities q_{ij} being easily found for any alternant hydrocarbon. Atom–atom polarizabilities are much more troublesome to calculate.

Table V compares σ-constants calculated by the *FM* method for 3' and 4'-substituted 4-biphenyl with the values estimated by Berliner and Blommers[8] from the dissociation constants of the cor-

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(12) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265, 275, 283 (1950).

(13) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," Centre National de la Recherche Scientifique, Paris, France.

(14) D. H. McDaniel and H. C. Brown, *Chem. Revs.*, **23**, 420 (1958).

TABLE IV

σ-CONSTANTS CALCULATED BY *FM* (*F′M′*) METHODS FOR NAPHTHALENE

Substituent	σ_{31}	σ_{41}	σ_{51}	σ_{61}	σ_{71}
NO_2	0.71 (0.70)	0.84 (0.84)	0.52 (0.51)	0.41 (0.41)	0.53 (0.52)
CN	.56 (.55)	.73 (.72)	.43 (.42)	.32 (.32)	.43 (.43)
Br	.39 (.40)	.19 (.19)	.22 (.23)	.23 (.21)	.21 (.22)
Cl	...	.19 (.20)	.21 (.22)	.23 (.19)	...
Me	...	− .21 (− .21)	− .07 (− .07)	− .04 (− .05)	−0.08 (−0.08)
MeO	...	− .42 (− .40)	− .05 (− .03)	.07 (.02)	− .07 (− .06)
HO	.12 (.15)	− .57 (− .62)	− .09 (− .06)	.07 (.01)	− .08 (− .10)
H_2N	...	− .87 (− .85)	− .29 (− .25)	...	...

responding biphenyl-4-carboxylic acids. The agreement is again satisfactory (standard deviation, 0.064 σ-unit). These values are also plotted in Fig. 2.

TABLE V

Substituent	$\sigma_{3'4}$ Obsd.	$\sigma_{3'4}$ Calcd.	$\sigma_{4'4}$ Obsd.	$\sigma_{4'4}$ Calcd.
O_2N	0.23	0.27	0.30	0.29
Br	0.12	0.15	.13	.15
Cl			.13	.15
Me			− .02	− .05
MeO			.07	− .04
HO			− .19	− .07
H_2N			− .25	− .19

Vaughan, *et al.*,[15] have measured the rates of alkaline hydrolysis of a number of substituted ethyl 1-naphthoates. Assuming the ρ-constant for this reaction to be the same as for the alkaline hydrolysis of substituted ethyl benzoates, and using the σ-constants listed in Table III, we can calculate the relative rate constants for the naphthoic esters. Table VI compares the calculated and observed rates. The agreement is good (standard deviation in log k/k_0, 0.12).

TABLE VI

COMPARISON OF RELATIVE RATES OF HYDROLYSIS OF SUBSTITUTED ETHYL 1-NAPHTHOATES CALCULATED BY THE *FM* TREATMENT WITH THOSE OBSERVED

Substituent	log k/k_0 (calcd.)	log k/k_0 (obsd.)
3-NO_2	1.56	1.57
3-Cl	0.86	0.83
3-Br	.82	.83
3-Me	− .15	− .15
4-NO_2	1.85	1.61
4-Cl	0.42	0.55
4-Br	.41	.58
4-Me	− .47	− .35
5-NO_2	1.14	1.14
6-NO_2	0.90	1.09

Table VII compares σ-constants derived from the *pK*'s of nitronaphthoic acids[1,16] and of naphthylamines[17] with those calculated from eq. 2 and 3. The agreement here is still satisfactory, especially in view of the considerable scatter shown (Table VII) by individual σ-constants derived from our measurements (*pK*'s of carboxylic acids in 50% ethanol) and from the measurements of Berliner and Winicov (*pK*'s of carboxylic acids in 50% butyl Cellosolve) or Bryson (*pK*'s of amines in water). The only serious discrepancies occur in the case of 4-nitro-1-naphthylamine (where there must be a large contribution from mutual conjugation between the amino and nitro groups) and of 8-nitronaphthalene-1-carboxylic acid (which is discussed below). The standard deviation for the naphthylamines,[17] omitting the 1,4-isomer, is 0.084 σ-unit.

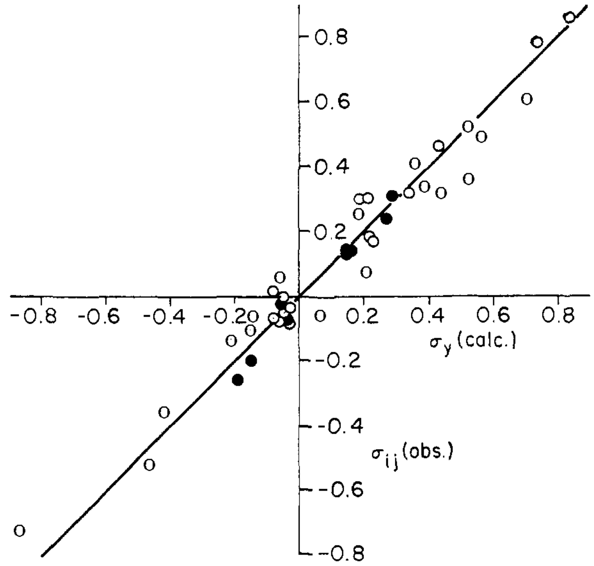

Fig. 2.—Plot of σ-constants calculated by the *FM* method *vs.* experimental values for naphthalene (○) and biphenyl (●).

In rigid aliphatic systems, where no mesomeric or π-inductive effects can operate, there should be a simple correlation between the σ-contants of substituents and the field constants *F* or *F′*. Very few suitable measurements have been reported, most of the data for saturated systems referring to flexible molecules where the mean distance between the substituent and the reaction center is uncertain, or to molecules where the substituent and reaction center are so close together that steric hindrance becomes a factor. A few measurements are, however, available[18] for the effects of substituents in the 4-position on the acidity of 2,2,2-bicyclooötane-1-carboxylic acid. Table VIII shows a comparison of the derived σ-constants with those calculated from eq. 2 and 3.

Discussion

The success of this simple treatment seems to justify our general approach, in particular our

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[15] A. Fischer, W. J. Mitchell, G. S. Ogilvie, J. Packer, J. E. Packer and J. Vaughan, *J. Chem. Soc.*, 1427 (1958).

[16] E. Berliner and E. H. Winicov, *J. Am. Chem. Soc.*, **81**, 1630 (1959).

[17] A. Bryson, *ibid.*, **82**, 4862 (1960).

[18] J. D. Roberts and W. T. Moreland, *J. Am. Chem. Soc.*, **75**, 2167 (1953).

TABLE VII

σ-CONSTANTS COMPARED WITH THEORETICAL VALUES

Subst.	σ-Constant	Ref. 1	Ref. 16	Ref. 17	*FM*	*F'M'*
NO_2	σ_{31}	0.61	0.64	0.63	0.71	0.70
	σ_{41}	.86	1.02	1.21	.84	.84
	σ_{51}	.54	0.68	0.39	.52	.51
	σ_{61}	.41	.53	.34	.41	.41
	σ_{71}	.36	.35	.44	.53	.52
	σ_{42}	..	.66	.58	.71	.70
	σ_{52}	..	.48	.37	.41	.42
	σ_{62}	..	.59	.52	.41	.39
	σ_{72}	..	.50	.34	.36	.36
	σ_{82}	..	.19	.48	.53	.57
CN	σ_{31}	.59	..	.56	.56	.55
	σ_{42}	..	..	.50	.56	.55
Cl	σ_{31}	..	..	.41	.38	.39
	σ_{51}	.29	..	.18	.21	.22
	σ_{61}	.17	..	.13	.23	.19
	σ_{71}	..	..	.13	.21	.21
	σ_{42}	..	..	.25	.38	.39
	σ_{72}	..	..	.13	.19	.18
Br	σ_{31}	.34	..	.40	.39	.40
	σ_{41}	.30	..	.21	.19	.19
	σ_{42}	..	..	.24	.39	.40
I	σ_{31}	..	..	.36	.35	.36
	σ_{42}	..	..	.24	.35	.36
MeOOC	σ_{31}	..	..	.26	.37	.38
	σ_{42}	..	..	.25	.37	.38
MeO	σ_{31}	..	..	.21	.12	.14
	σ_{61}	−.06	..	.01	.07	.02
	σ_{71}	−.08	..	−.08	−.07	−.06
	σ_{42}	..	..	.02	.12	.14
	σ_{62}	..	..	−.18	−.10	−.08
	σ_{72}	..	..	−.01	.06	.04
HO	σ_{31}	.06	..	.20	.12	.15
	σ_{51}	−.06	..	−.03	−.09	−.06
	σ_{61}	−.08	..	−.04	.07	.01
	σ_{71}	−.10	..	−.18	−.08	−.10
	σ_{52}	..	..	.01	.07	.04
	σ_{72}	..	..	−.08	.06	.04
Me	σ_{31}	..	..	−.04	−.07	−.10

TABLE VIII

Substituent	σ_{41} obsd.	σ_{41} calcd. (*FM*)	σ_{41} calcd. (*F'M'*)
HO	0.27	0.13	0.08
EtOOC	.28	.32	.33
Br	.43	.34	.33
NC	.55	.49	.50

assumption that the σ-inductive effect of a substituent is unimportant at atoms separated from it by more than one bond.

The constants listed in Table III are of interest in connection with the problem of hyperconjugation. If the field effect of a substituent depended only on the charge at the adjacent atom in the ring, the π-inductive effect would be proportional to the field effect. The fact that M/F or M'/F' is much greater for alkyl groups than for NO_2, CN or Me_3N^+ would then imply a significant mesomeric contribution (*i.e.*, hyperconjugation). However the assumption probably is not correct. The field effect of NO_2, CN or Me_3N probably is due mainly to charges on the substituent itself. If the σ-inductive effect is indeed insignificant, the charge on the ring atom adjacent to the substituent would then be small—and consequently the π-inductive effect would also be small. On the other hand, the field effect of alkyl must be due mainly to charges set up at the adjacent ring atom since alkyl groups carry no formal charge. Since the π-inductive effect is determined only by the charge on the ring atom adjacent to the substituent, and since in the case of inductive substituents the parameters M, F or M', F' are measures of the π-inductive and field effects, respectively, the ratio M/F or M'/F' should be much greater for alkyl than for charged or dipolar groups such as NO_2, CN or Me_3N^+.

Similar criticisms can be directed at the arguments for hyperconjugation put forward by Taft and Lewis[19] based on their subdivision of substituent effects into inductive and resonance contributions. Their "resonance effect" would include contributions of uncertain magnitude from the π-inductive effect; the "hyperconjugation" of alkyl groups might be due entirely to this.

The treatment described here is limited to cases where mutual conjugation is unimportant and to reactions where the substrate to which the substituent is attached undergoes no drastic reorganization. These are the conditions that must be met if the Hammett equation is to hold good. If they are not met, the Hammett equation must be replaced[2] by the more general relation

$$\log k/k_0 = \rho\sigma + \rho'\sigma' \qquad (4)$$

where ρ', σ' are measures of the response of the reaction center and substituent to mutual conjugation. In our treatment σ' would be given approximately by

$$\sigma_{ij}' = Eq_{ij} \qquad (5)$$

or

$$\sigma_{ij}' = E'\pi_{ij} \qquad (6)$$

where the electromeric parameters E, E' could be determined empirically from data for benzene. At present there would be little point in doing this, however, since there are not enough data for other molecules to check the validity of such an approach.

For the same reason we feel that attempts to refine our treatment would be pointless at present, although there are several obvious ways in which it might be improved.

(a) Our method for calculating the field effect of substituents is clearly very crude. It would perhaps be better to use the Kirkwood–Westheimer approach, treating the molecule as a cavity of low dielectric constant in a medium of high dielectric constant and calculating the electrostatic field of the substituent as a dipole (or multipole) field. The greatest difference from our treatment would arise in cases where the line joining the substituent to the reaction center passes near the edge of the cavity; here our treatment should predict too large a contribution by the field effect—and the experimental data show this to be the case (*cf.* the calculated and observed values for σ_{71} and σ_{82}, Table VII). There should also be significant changes in the field effect with solvent; this may account for the differences between the σ-constants for naphthalene estimated in different ways (Table VI). Calculations by the Kirkwood–

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(19) R. W. Taft and I. C. Lewis, *Tetrahedron* **5**, 210 (1959).

Westheimer method would, however, be difficult to carry out for substituted naphthalenes and the method is in any case subject to uncertain errors through its treatment of the solvent as a uniform dielectric.

(b) The calculation of the π-inductive and mesomeric effects could be carried out by more refined procedures such as the SCF MO method. Calculation of this kind are in progress here though we doubt if the results will differ much from those given by the simple perturbation treatment.

(c) The charges set up in an adjacent conjugated system through polarization of the π-electrons by a substituent (π-inductive and mesomeric effects) should influence a reaction center directly by the field effect. Thus the charge set up in the positions *o:p* to a +E or −E substituent in benzene should in this way affect a reaction center at the *meta* position. This relayed mesomeric–field effect would simulate a resonance interaction directed to the positions *meta* to the substituent. Taft[20] has claimed that such interactions are important in benzene.

However, the main need at present is for more data on the effects of substituents in rigid molecules of known geometry, other than benzene. Any attempt to build up a more elaborate theory until such data are forthcoming seems to us a useless exercise.

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[20] See R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959); R. W. Taft, S. Ehrenson, I. C. Lewis and R. E. Glick, *ibid.*, **81**, 5352 (1959).

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Carbon as a Hydrogen Bonding Base and Carbon–Hydrogen–Carbon Bonding

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One-to-one hydrogen bonding between hydrogen donors and the isocyanide group is demonstrated by infrared and nuclear magnetic resonance spectra and concentration dependencies of the bonded species. Electronic and steric arguments as well as experimental evidence are presented to prove that the hydrogen bond is at carbon. Proof is given for a carbon–hydrogen–carbon bond between an isocyanide and the C–H in an acetylene. Frequency shift and equilibrium data indicate that isocyanides (carbon sp-bonding) form hydrogen bonds of comparable strength to cyanides (nitrogen sp-bonding).

In an earlier communication a hydrogen bond to an isocyanide[1a,b] and a carbon–hydrogen–carbon[1a] bond were announced. Detailed evidence of the points made in the communication and new evidence are given in this paper to show that isocyanides form hydrogen bonds and that these bonds are at the carbon atom. In a similar manner carbon–hydrogen–carbon bonding is demonstrated. For both types of bonding data are presented to show first that bonding occurs; second that it is at carbon; and third that bonding at sp-carbon is comparable to bonding at sp-nitrogen.

Proof of Hydrogen Bond Formation.—The presence of equilibrium 1 is demonstrated by infrared spectral evidence. An intense, characteristic ν_s for bonded OH appears at 3483 cm.$^{-1}$

$$n\text{-}C_5H_{11}OH + C_6H_5CH_2NC = (n\text{-}C_5H_{11}OH)(C_6H_5CH_2NC) \quad (1)$$

when *n*-amyl alcohol is added to benzyl isocyanide although this band is absent in both reactants (Fig. 1). Furthermore, the intensity of the new band is directly proportional to the concentration of each of the reactants, indicating that one molecule of each participates in the bonded complex. With appropriate concentration changes the new band grows at the expense of free OH and alcohol–alcohol bonded OH bands.

Nuclear magnetic resonance (n.m.r.) spectra also demonstrate the existence of a hydrogen bond between alcohols and benzyl isocyanide. With methanol, at concentrations favoring bonding, the hydroxyl proton moves to lower field. But even more striking is the occurrence of splitting of the hydroxyl proton (quartet) and of the methyl protons (doublet) at about 1:1 methanol to benzyl isocyanide. This is good evidence for a long-lived bond between the two.

Bonding to isocyanides by a hydrocarbon is shown by similar evidence. Figure 2 shows the infrared data. Phenylacetylene dissolved in benzyl isocyanide shows an acetylenic C–H ν_s at 3284 cm.$^{-1}$. This band is 26 cm.$^{-1}$ lower than the normal acetylenic C–H ν_s at 3310 cm.$^{-1}$. This is a small shift[2] but it is similar to the shift in benzonitrile (32 cm.$^{-1}$). When a solution of phenylacetylene in benzyl isocyanide is diluted with carbon tetrachloride the normal band at 3310 cm.$^{-1}$ returns but a slight shoulder remains about 26 cm.$^{-1}$ lower than the major peak, characteristic of a mixture of free and bonded C–H.

In n.m.r. a hydrogen bond between phenylacetylene and benzyl isocyanide is shown by a shift of the acetylenic proton to lower field. In pure phenylacetylene this proton precesses at 153 cycles per second (2.53 δ) relative to tetramethylsilane. At a benzyl isocyanide concentration of 0.475 mole fraction this peak is at 163 cycles per second while the aromatic proton major peak moves only from 402 to 406 cycles per second. The acetylenic proton peak of phenylacetylene at infinite dilution in benzyl isocyanide occurs at 169 cycles per second. A plot of this shift *versus* mole fraction of the two

[1] (a) L. L. Ferstandig, *J. Am. Chem. Soc.*, **84**, 1323 (1962). (b) Isocyanide hydrogen bonding was also discovered independently by P. v. R. Schleyer and A. Allerhand, *ibid.*, **84**, 1322 (1962).

[2] R. West and C. S. Kraihanzel, *ibid.*, **83**, 765 (1961).