method described for the 3-cyano isomer (64% yield). It crystallized from petroleum ether in white needles, m.p. 159–160°.

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.9; H, 4.3. Found: C, 74.0; H, 4.3.

7-Cyano-1-naphthoic Acid.—The methyl ester was hydrolyzed by the method described for the 3-isomer giving **7-cyano-1-naphthoic acid**, white needles from dilute ethanol, m.p. 277–279° dec.

Anal. Calcd. for $C_{12}H_7NO_2$: C, 73.1; H, 3.6; N, 7.1. Found: C, 73.3; H, 3.8; N, 7.0.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, QUEEN MARY COLLEGE, LONDON]

Substituent Effects. III.[1] Acid Dissociation Constants of Substituted 1-Naphthoic Acids and Carbonyl Stretching Frequencies of Their Esters

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The apparent dissociation constants of thirty-three substituted 1-naphthoic acids in 50% v./v. ethanol-water have been determined, and substituent constants calculated using Hammett's equation. These are correlated with the shifts in the infrared spectra of the carbonyl stretching frequencies of the corresponding methyl esters.

The preparations of the naphthoic acids have been described in the previous papers. The esters were either samples prepared in the synthesis and purifications of the acids, or were obtained by treatment of the acids with excess diazomethane in ether.

Various attempts were made to determine the relative strengths of the naphthoic acids. All were based on the Henderson–Hasselbalch equation (1)

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{residual acid}]} \qquad (1)$$

This relates the *p*H of a dilute partially neutralized aqueous solution of a weak acid with the degree of neutralization. In a dilute aqueous organic system a similar relation may be assumed and if such a solution is 50% neutralized, the apparent *p*H will be a measure of the acid strength in that solvent.

It was hoped to employ the spectrophotometric method of Flexser, Hammett and Dingwall[3] to determine the log ratio in various buffered solutions of the acids; however the positions and extinction coefficients of suitable peaks in the ultraviolet spectra were too similar in solutions of the salt and the free acid to give reliable and accurate results.

The second method of approach was by potentiometric titration of the acids using a glass and saturated calomel electrode system in 50% ethanol–water. Each titration took about 90 minutes during which time the electrodes were affected by the solvent since changes in the *p*H readings as large as 0.06 *p*H unit occurred in standard buffers before and after such titrations. Such behavior is to be expected in non-aqueous systems,[4] and it was decided to expose the electrodes to the organic solvents for the minimum time. The readings as the calculated half neutralization point of a solution of the acid in 50% ethanol (by volume) on the *p*H scale of a Doran Universal *p*H meter were therefore taken as the acid strengths or *pK* values. The meter was calibrated with aqueous buffers and no correction was made for liquid junction potentials. The method employed for these determinations depended for its accuracy on the assumption that the acids were exactly 50% neutralized, in turn depending on three conditions: (1) The sodium hydroxide used in the neutralizations was of exactly known strength. (2) The titration errors were zero. (3) The acids were 100% pure.

Errors from the first two sources may be easily estimated. Errors from the last source are difficult to estimate. Complete potentiometric titrations on several of the acids indicated a purity of better than 99.7%, but this does not mean that isomeric acids or acids of similar molecular weight were not present. However, the errors due to this should have been small since such impurities should be of similar acid strength.

Using standardized carbonate-free sodium hydroxide and calibrated micro-burets fitted with carbon dioxide guard tubes in the titrations, the errors from these three sources were estimated at 0.005 *p*H unit, considerably less than the observed deviations (0.01–0.03 *p*H unit) which are undoubtedly due to the errors inherent in the glass electrode.

The results of the *pK* measurements are given in Table I. The value observed for benzoic acid agrees favorably with those already available.[5] These values were used to calculate the substituent constants σ_{ij} (j = position of side chain, and i = position of substituent), listed in Table II, by the direct application of the Hammett equation.[6]

$$\log K - \log K_0 = \rho\sigma_{ij} \qquad (1)$$

Here K and K_0 refer to the substituted and unsubstituted 1-naphthoic acid, respectively, and ρ has

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(1) Part II, preceding paper, *J. Am. Chem. Soc.*, **84**, 3541 (1962).

(2) George Herbert Jones Laboratory, University of Chicago, Chicago 37, Ill.

(3) L. A. Flexser, L. P. Hammett and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

(4) R. G. Bates, "Electrometric *p*H Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 252.

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TABLE I

pK VALUES OF SUBSTITUTED 1-NAPHTHOIC ACIDS $X-C_{10}H_6CO_2H$ IN 50% V./V. ETHANOL/WATER

Substituents	No. of determn.	Average *pK*	Max. devn.	Median devn.
0	22	5.54	0.02	0.01
$3-NO_2$	5	4.61	.01	.01
$4-NO_2$	5	4.23	.02	.01
$5-NO_2$	5	4.72	.03	.02
$6-NO_2$	5	4.92	.02	.01
$7-NO_2$	5	4.99	.02	.01
3-CN	5	4.64	.02	.01
4-CN	5	4.34	.03	.02
5-CN	5	4.84	.01	.01
6-CN	3	5.04	.01	.01
7-CN	3	5.07	.01	.01
3-Br	5	5.02	.02	.01
4-Br	5	5.09	.01	.01
5-Br	5	5.09	.01	.01
6-Br	5	5.26	.01	.01
7-Br	5	5.43	.01	.01
4-Cl	2	5.15	.02	.02
5-Cl	5	5.10	.02	.01
6-Cl	5	5.29	.02	.01
4-Me	5	5.75	.01	.01
5-Me	3	5.52	.00	.00
6-Me	5	5.61	.01	.01
7-Me	5	5.65	.01	.01
4-MeO	5	6.09	.02	.02
5-MeO	3	5.56	.01	.01
6-MeO	5	5.63	.03	.02
7-MeO	5	5.66	.02	.01
3-OH	5	5.45	.01	.01
4-OH	3	6.33	.01	.01
5-OH	5	5.64	.01	.01
6-OH	5	5.66	.03	.01
7-OH	3	5.69	.01	.01
$4-NH_2$	3	6.63	.02	.01
$5-NH_2$	3	5.74	.03	.01
Benzoic acid	5	5.74	.02	.01

TABLE II

σ_{ij} VALUES FOR NAPHTHALENE ($j = 1$)

Substituent	$i = 3$	$i = 4$	$i = 5$	$i = 6$	$i = 7$
NO_2	0.61	0.86	0.54	0.41	0.36
CN	.59	.79	.46	.34	.31
Cl	..	.26	.29	.17	..
Br	.34	.30	.30	.18	.07
Me	..	− .14	.01	− .05	− .07
MeO	..	− .36	− .01	− .06	− .08
OH	.06	− .52	− .06	− .08	− .10
NH_2	..	− .72	− .13	..	..

the value assigned for the benzoic acids in the solvent being used, 1522.[7]

The carbonyl stretching frequencies of a number of substituted methyl naphthoates in chloroform solution have also been determined to study their correlation with the σ_{ij} values. The frequencies and shifts from the unsubstituted compounds are given in Table III. All measurements are in wave numbers, the estimated limits of error being ±0.5 cm.$^{-1}$. The correlation between these shifts and the σ_{ij} values is shown graphically in Fig. 1. Although the shifts are small, there appears to be a good correlation as is also the case in the benzene system.[7] The standard deviation for the compounds listed in Table III is 1.1 cm.$^{-1}$.

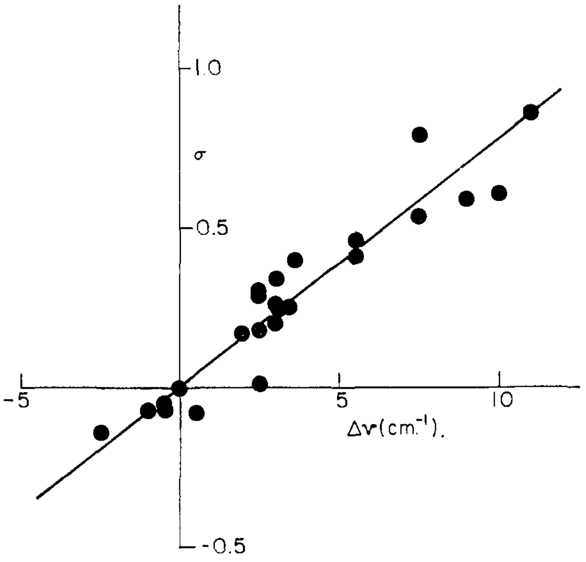

Fig. 1.—Plot of shifts (Δν) in infrared carbonyl frequencies of methyl naphthalenecarboxylates *vs.* σ-constants of substituents.

TABLE III

INFRARED CARBONYL STRETCHING FREQUENCIES OF SUBSTITUTED METHYL NAPHTHOATES, $X-C_{10}H_6CO_2Me$

Scanning speed, 1μ/8-min.; solvent, chloroform, concn., 0.7%; cell, 0.13 mm.

Substituent	Wave length, μ	Wave no., cm.$^{-1}$	Shift, Δν
0	5.841	1712.0	0.0
$3-NO_2$	5.807	1722.0	+10.0
$4-NO_2$	5.803	1723.0	+11.0
$5-NO_2$	5.815	1719.5	+ 7.5
$6-NO_2$	5.822	1717.5	+ 5.5
$7-NO_2$	5.828	1716.0	+ 4.0
3-CN	5.810	1721.0	+ 9.0
4-CN	5.815	1719.5	+ 7.5
5-CN	5.823	1717.5	+ 5.5
6-CN	5.831	1715.0	+ 3.0
7-CN	5.833	1714.5	+ 2.5
3-Br	5.833	1714.5	+ 2.5
4-Br	5.834	1714.0	+ 2.0
5-Br	5.832	1714.5	+ 2.5
6-Br	5.832	1714.5	+ 2.5
7-Br	5.836	1713.5	+ 1.5
4-Cl	5.831	1715.0	+ 3.0
5-Cl	5.833	1714.5	+ 2.5
6-Cl	5.835	1714.0	+ 2.0
4-Me	5.850	1709.5	− 2.5
5-Me	5.832	1714.5	+ 2.5
6-Me	5.843	1711.5	− 0.5
7-Me	5.844	1711.0	− 1.0
4-MeO	5.855	1708.0	− 4.0
5-MeO	5.840	1714.0	+ 0.0
6-MeO	5.842	1711.5	− .5
7-MeO	5.839	1712.5	+ .5

Values for certain of these σ-constants have been estimated from data for the *pK*'s of nitronaphthoic

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(7) H. H. Jaffé, *Chem. Revs.*, **53**, 241 (1953).

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.

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Substituent Effects. IV.[1] A Quantitative Theory

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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

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