N-benzoyl derivative, m.p. 160–161° alone and when mixed with an authentic sample. Distillation of extract 2 gave 5.0 g. (21.4%) of aniline, b.p. 100–103° at 58.5 mm.

Phenylation of Diethyl Malonate.—Sodium amide (2.0 moles), diethyl malonate (1.0 mole, 160.2 g.) and bromobenzene (0.5 mole, 78.6 g.) were allowed to react using the procedure described above for the phenylation of ethyl acetate. Distillation of the combined acidic extracts gave 94.7 g. of recovered diethyl malonate, b.p. 93–95° at 16 mm., and 60.4 g. (51.2%) of diethyl phenylmalonate, A, b.p. 124–127° at 1.5 mm.[13] Distillation of the basic ether extracts gave 8.2 g. (17.6%) of aniline, b.p. 104–105° at 60 mm. That compound A is diethyl phenylmalonate was shown in the following ways: (1) molecular weight determinations by the saponification equivalent method[14] gave values of 235.16, 239.96 and 240.36; calcd. mol. wt. of A is 236.26; (2) A mixture of A, urea and sodium ethoxide in anhydrous ethanol was heated in a sealed tube at 115° for three hours according to the procedure described[13] for similar reactions to give 5-phenylbarbituric acid, m.p. 260.5–261.5°, from hot water[15]; (3) A mixture of potassium hydroxide (0.36 mole, 20.0 g.) in 20 ml. of water and A (0.1 mole, 23.6 g.) was refluxed for two hours. Then, 20 ml. of water was added and 20 ml. of liquid was distilled to remove the ethanol which was formed. Then, concentrated sulfuric acid (0.33 mole, 32 g.) was added slowly. The mixture was refluxed for an additional three hours and then was cooled to room temperature. It was made strongly basic with aqueous potassium hydroxide, extracted with several portions of ether and the extracts were discarded. The residue was acidified with dilute sulfuric acid and extracted with several portions of ether. The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed to give 8.2 g. (60.3%) of phenylacetic acid, m.p. 77.0–77.8° alone and when mixed with an authentic sample. This procedure is a modification of that described[16] for the conversion of diethyl *sec*-butylmalonate to 3-methylpentanoic acid.

Phenylation Followed by Ethylation of Malonic Esters. (a) Diethyl Malonate.—The last reaction was repeated except that ethyl bromide (1.0 mole, 109.0 g.) was added after the addition of the bromobenzene was completed. The reaction mixture was stirred for an additional 15 minutes and was then processed as described above. Distillation of the combined acidic extracts gave 108.5 g. of a mixture of bromobenzene and diethyl malonate, b.p. 100–127° at 59.3 mm., and 64.4 g. of a mixture of diethyl phenylmalonate and diethyl ethylphenylmalonate, b.p. 130–140° at 2.6 mm. (mixture A). From the basic extract there was obtained 12.7 g. of N-ethylaniline, b.p. 126–131° at 63.5 mm. (lit.[17] 123.6° at 60.0 mm.); N-benzoyl derivative, m.p. 59.0–60.0 alone and when mixed with an authentic sample. The average molecular weight of mixture A was 258.03 (based on three determinations). Therefore, mixture A consists of 20.5% of diethyl phenylmalonate (calcd. mol. wt. 236.26) and 79.5% of diethyl ethylphenylmalonate (calcd. mol. wt. 264.31) and thus the actual yield of the former ester is 11.2% and that of the latter ester is 38.8%.

(b) Dimethyl Malonate.—The last reaction was repeated except that the diethyl malonate was replaced by dimethyl malonate (1.0 mole, 132.0 g.). Processing the reaction mixture gave 22.4 g. (21.5%) of dimethyl phenylmalonate, b.p. 131.0–133.5° at 5.0 mm., m.p. 51.2–52.2°[18]; 22.4 g. (25.3%) of phenylmalonamide, m.p. 230–233° alone and when mixed with an authentic sample[19]; and 13.0 g. (21.4%) of N-ethylaniline, b.p. 122–127° at 59.0 mm.[17]

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[13] W. L. Nelson and L. H. Cretcher, THIS JOURNAL, **50**, 2758 (1928).

[14] S. Siggia, "Quantitative Organic Analysis Via Functional Groups," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 46.

[15] H. J. Morsman, *Helv. Chim. Acta*, **18**, 1254 (1935).

[16] E. B. Vliet, C. S. Marvel and C. M. Hsueh, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 416.

[17] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

[18] A. H. Wallingford, A. H. Homeyer and D. M. Jones, THIS JOURNAL, **63**, 2056 (1941).

[19] A. W. Dox and L. Yoder, *ibid.*, **44**, 1564 (1922).

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[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Dissociation Constants of Nitronaphthoic Acids[1]

BY ERNST BERLINER AND EDITH H. WINICOV[2]

RECEIVED SEPTEMBER 13, 1958

The dissociation constants of 13 nitronaphthoic acids have been determined potentiometrically at 25° in 50% aqueous butyl Cellosolve. The results are discussed in terms of conjugation in the naphthalene system. A set of σ-values has been derived from the dissociation constants.

Although far more attention has been paid to substituent effects in the benzene than in the naphthalene series, there has been some activity in recent years in the study of substituted naphthalenes. As a contribution to this latter field, we wish to report the dissociation constants of nitronaphthoic acids. The main purpose of this study was to learn something about the extent of conjugation among the various positions in napthalene and the transmission of substituent effects; but substituent constants for the differently situated nitro groups, comparable to those in the benzene series, have also been established. Some σ-constants for nitro groups on naphthalene have previously been reported and will be referred to below.

It was particularly important to determine the dissociation constants of as many of the acids as possible, and under the same set of conditions, because only then can a coherent picture be obtained. Of the 14 possible nitronaphthoic acids, only 3-nitro-2-naphthoic acid could not be prepared, and hence the study included 13 nitronaphthoic acids, as well as the two unsubstituted ones.[3] The solvent was 50% by volume aqueous butyl Cellosolve, which was chosen because of the low solubility of some of the acids, and because values for the dissociation constants of substituted benzoic acids are available in the same solvent.[4]

Results and Discussion.—The dissociation constants were determined at 25° by potentiometric titration, using a Beckman model G *p*H meter. They were determined in triplicate, except for 7-

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[1] Taken from a dissertation submitted by Mrs. E. H. Winicov to the Graduate School of Bryn Mawr College in partial fulfillment of the requirements for the Ph.D. degree, June, 1958.

[2] Eastman Kodak Fellow 1956–1957.

[3] We are very much indebted to Dr. J. Vaughan of the University of Canterbury, Christchurch, New Zealand, for the sample of 2-nitro-1-naphthoic acid; see R. D. Topsom and J. Vaughan, *J. Chem. Soc.*, 2842 (1957).

[4] E. Berliner and E. A. Blommers, THIS JOURNAL, **73**, 2479 (1951).

nitro-2-naphthoic acid, of which only a small sample was available. The values are reported in Table I, which also contains the estimated errors and values ΔpK, which are differences in pK between the nitro-substituted and the appropriate unsubstituted acid. They are a measure of the effect of the nitro group on the particular acid.

TABLE I

APPARENT DISSOCIATION CONSTANTS OF NITRONAPHTHOIC ACIDS IN 50% (BY VOLUME) AQUEOUS BUTYL CELLOSOLVE AT 25°

Acid	pK	Av. dev.	ΔpK
1-Naphthoic	5.89	0.01	0.00
2-Nitro-1-naphthoic	3.96	.03	1.93
3-Nitro-1-naphthoic	5.00	.02	0.89
4-Nitro-1-naphthoic	4.47	.01	1.42
5-Nitro-1-naphthoic	4.95	03	0.94
6-Nitro-1-naphthoic	5.15	.02	.74
7-Nitro-1-naphthoic	5.40	.02	.49
8-Nitro-1-naphthoic	5.25	.03	.64
2-Naphthoic	5.95	.02	0.00
1-Nitro-2-naphthoic	4.53	.01	1.42
4-Nitro-2-naphthoic	4.97	.02	0.98
5-Nitro-2-naphthoic	5.23	.02	.72
6-Nitro-2-naphthoic	5.07	.01	.88
7-Nitro-2-naphthoic	5.19		.76
8-Nitro-2-naphthoic	5.63	.01	.32
Benzoic	5.89	.02	

All nitro-substituted acids are stronger than the unsubstituted ones, and the homonuclear substituted ones, *i.e.*, those with the nitro and the carboxyl groups in the same ring, are generally more acidic than the heteronuclear ones. 1-Naphthoic acid is stronger than 2-naphthoic acid, as has also been observed in water[5] and in 78.1% ethanol.[6,7]

The simplest theoretical model by which to predict the effect of substituents in naphthalene is the one that obtains on writing first-excited contributing structures, the quinoid structures, which divide the positions into conjugated and non-conjugated ones. Substituents in conjugated positions should interact more strongly, and acids derived from them should be stronger than those where substituents are in non-conjugated positions. Of the 1-naphthoic acids, those with a nitro group in the 2-, 4-, 5- and 7-positions should be stronger, of the 2-naphthoic acids those with a nitro group in positions 1, 3, 6 and 8. The agreement is not bad, except that in each set there is one acid which shows no enhancement whatever, although the nitro groups are in conjugated positions, namely 7-nitro-1-naphthoic acid and 8-nitro-2-naphthoic acid. These acids are, in fact, the weakest in their respective sets and weaker than all the non-conjugated ones. This must be a peculiarity of the present system, rather than a failure of the well established model, because in the nitronaphthylamines,[8] and presumably also the nitronaphthols,[9] the two corresponding compounds show the expected increased effect of conjugation. In both the amines and the naphthols conjugative interaction would be expected, however, to be stronger than in the acids. The conjugated homonuclear acids are all stronger than the heteronuclear ones, probably because the heteronuclear substituents are in conjugation with each other only at the expense of the stabilizing energy of a complete benzene ring.[10]

For a somewhat more detailed discussion it is helpful to arrange the data as shown in Fig. 1,

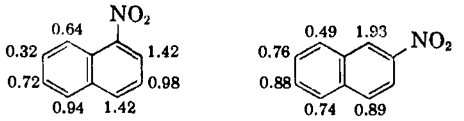

Fig. 1.—Apparent charge distribution in nitronaphthalenes from the ionization of nitronaphthoic acids.

where the emphasis is on the effect of the nitro group. The numbers are the ΔpK values obtained from the appropriate acids and can be considered a measure of the electron deficiency created by the 1- or 2-nitro group in the positions around the ring. From these diagrams, the following appears to be the effect of the nitro groups. The 2-nitro group creates a large electron deficiency at the 1-position, charges of about one-half this magnitude at the 4- and 6-positions, somewhat smaller deficiencies at the non-conjugated positions 5 and 7, but least in the conjugated 8-position. The 1-nitro group creates the largest positive charge in the 2- and 4-positions, the two values being equal but less than the one created by the 2-nitro group in the 1-position. Approximately equal effects are obtained for position 3 and the conjugated position 5, smaller effects in 6 and 8, and least in position 7. The considerable effects in the non-conjugated *meta* positions (1,3 and 2,4) arise from inductive effects, which should be stronger when the substituents are in the same ring, hence these positions are more affected than even the conjugated heteronuclear ones. Compared to the effect in these two positions, the transmission from position 1 to 8, which are also *meta* positions, is noticeably smaller, which may be due to steric influences (see below). A combination of inductive and conjugation effects causes the small variations in the heteronuclear positions, although it is observed that in three of the heteronuclear, non-conjugated positions (1,6-, 2,5- and 2,7-) the nitro groups have practically identical effects (ΔpK about 0.74), while in the fourth (1,8-) the effect is only slightly less (0.64).[11,13]

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[5] J. F. J. Dippy, S. R. C. Hughes and J. W. Laxton, *J. Chem. Soc.*, 1470 (1954).

[6] S. Oae and C. C. Price, THIS JOURNAL, **79**, 2547 (1957).

[7] But in these solvents 1-naphthoic acid is stronger than benzoic acid, although less so in aqueous ethanol than in water, whereas in 50% aqueous butyl Cellosolve the two acids are of the same strength. This is probably a specific consequence of the solvent, because the unusually large variation in pK of 1-naphthoic acid, relative to the variations observed in other acids, on going from water to the similar solvent, 60% aqueous butyl carbitol (diethylene glycol mono-*n*-butyl ether), has been commented on by J. O. Halford, who stated ". . . We are therefore unable to decide as to which of the three acids, benzoic, acetic and 1-naphthoic acid is intrinsically the strongest"; THIS JOURNAL, **53**, 2944 (1931).

[8] A. Bryson, *Trans. Faraday Soc.*, **45**, 257 (1949); **47**, 522 (1951).

[9] A. Bryson, quoted by P. R. Wells and E. R. Ward, *Chemistry & Industry*, 528 (1958).

[10] K. C. Schreiber and M. C. Kennedy, THIS JOURNAL, **78**, 153 (1956).

[11] The simple valence bond description, using only contributing structures, does not provide a quantitative estimate as to the expected differences among the conjugated acids. If there is a relation between the coefficients of all contributing structures in the hydrocarbon and the extent of conjugation in its derivatives, the rigorous valence bond solution of naphthalene (J. Sherman, *J. Chem. Phys.*, **2**, 488 (1934)) pre-

To what extent these relative experimental orders are really due to electronic interactions and not to secondary factors cannot be easily answered. It is clear that for a fuller understanding of substituent effects in naphthalene one must take into account the various possibilities for steric factors, which will obscure electronic interactions and will reflect themselves in dissociation constants and any substituent constants derived from them. In disubstituted naphthalenes generally, there are only two out of fourteen compounds where the two substituents are not *ortho* or *peri* to each other, or where one is not *peri* to a hydrogen. Either the functional group or the substituent may be forced out of the plane of the carbon framework with consequences which will be different for different reactions and different substituents. The lack of coplanarity of the carboxyl group in 1-naphthoic acid is believed to account partly for its greater acid strength,[14] although partly it is also due to the greater electronegativity of the 1- than the 2-naphthyl group.[15] This particular effect is present in all substituted 1-naphthoic acids as well. On the other hand, 2-nitro-1-naphthoic acid is stronger than 1-nitro-2-naphthoic acid, probably because of lack of coplanarity and consequent partial loss of conjugation of the 1-nitro group.[16,17] Classical steric hindrance is also more severe than in the benzene series; for instance, ethyl *o*-nitrobenzoate is hydrolyzed faster than ethyl benzoate,[18] but both ethyl 2-nitro and 8-nitro-1-naphthoate are saponified considerably slower than the unsubstituted ester,[19] although the corresponding acids are stronger than 1-naphthoic acid. In addition to these effects which, by changing the geometry of the substituents, alter their effective polarity, there must be specific hindrance to solvation of substituents in hindered positions, which, in turn, will modify their polar influences. In 1,8-derivatives, and possibly also in 1,7- and 2,8-compounds, there also exists the possibility for the special effects which have been discussed by Hammond with reference to ionization reactions,[20] namely the exclusion of solvent molecules and changes in the effective dielectric constant of the medium through which polar effects are transmitted. Such factors may, in fact, be responsible for the abnormally low values observed for the pK of the 1,7- and 2,8-acids. The over-all picture of substituent effects in naphthalene is therefore considerably more complex than in the benzene series.

Substituent Constants.—Various authors[21] have determined and compiled substituent constants for nitro groups in naphthalene, but there is some confusion about what to choose as log k_0. Some have used benzene derivatives as the standard, while others have chosen the appropriate unsubstituted naphthalene derivative. There is merit in referring the constants back to naphthalene, as was first suggested for a specific case by C. C. Price, *et al.*, who pointed out that all 1-naphthoates, including the unsubstituted one, are hydrolyzed slower than expected on the basis of the pK's of the acids, because of steric hindrance to saponification by the fused ring.[22] Hence a better agreement between pK's and rate constants is obtained when σ's are calculated from unsubstituted ethyl 1-naphthoates as a standard, rather than benzoate. In this paper, we propose to refer all σ-values to benzoic acid. This will avoid the confusion which may result from the addition of two more differently defined sets of σ-values to the already growing number, and also follows the recent plea for a return to a uniform set of σ's derived from substituted benzoic acids.[23] While this treatment may not always give a better agreement between σ's derived from different reactions, it may prove more illuminating.

The σ-constants thus defined are substituent constants for benzene derivatives where one of the substituents is a bridge, $(CH)_4$, fused either to the 2,3- or the 3,4-positions of the benzene ring; the other is a nitro group, which may be on the fused bridge or the benzene ring. It can readily be shown that these constants are sums of two constants, containing in every case also the value for the unsubstituted naphthalene compound as a constant contribution.[24,25] Since all 1-naphthalene derivatives are *o*-substituted benzenes, it is perhaps questionable if the Hammett equation[26] is expected to apply, but such compounds can be considered as having a constant *o*-substituent (except for 8-substituted derivatives), for which cases the relationship has been

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dicts the conjugation to be in the relative order 1,4 > 1,7 = 2,8 > 1,5 > 2,6. With the exception of the 1,7- and 2,8-acids, which are anomalously low and will not agree with any model, this is the experimentally observed order. However, in the nitronaphthylamines (ref. 8), and probably also the nitronaphthols (ref. 9), the dissociation constants indicate that a 6-nitro group has more effect on the 2-position, than a 5-nitro group has on the 1-position. The same is true in the alkaline hydrolysis of nitroacetnaphtalides (ref. 12); see also ref. 13.

(12) L. H. Krol, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **71**, 545 (1952); see also, P. van Berk, P. E. Verkade and B. M. Wepster, *ibid.*, **76**, 286 (1957).

(13) The charge distribution in the naphthylmethyl carbonium ions, which are electronically somewhat similar to the nitronaphthalenes, shows a slightly greater charge in the 6-position of the 2-ion, than in the 5-position of the 1-ion, as calculated by Dewar's simplified molecular orbital treatment (see for instance, M. J. S. Dewar in J. W. Cook, "Progress in Organic Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1953, p. 1). For homonuclear charges, this model predicts, for the carbonium ions, the sequence 2,1 > 1,2 = 1,4, where the position of the ion is listed first and the affected position second. This parallels the relative acid strength of the nitronaphthoic acids.

(14) See for instance, H. C. Brown, D. H. McDaniel and O. Häfliger in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 567.

(15) H. Schenkel, *Experientia*, **4**, 383 (1948).

(16) For a similar case see, E. Berliner, M. J. Quinn and P. J. Edgerton, THIS JOURNAL, **72**, 5305 (1950).

(17) See, however, ref. 13, where the same relative order is accounted for without recourse to steric inhibition of resonance.

(18) D. P. Evans, J. J. Gordon and H. B. Watson, *J. Chem. Soc.*, 1430 (1937).

(19) A. Fischer, W. J. Mitchell, G. S. Ogilvie, J. Packer, J. E. Packer and J. Vaughan, *ibid.*, 1426 (1958); A. Fischer, J. D. Murdoch, J. Packer, R. D. Topsom and J. Vaughan, *ibid.*, 4358 (1957).

(20) G. S. Hammond in M. S. Newman, "Steric Effects In Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 425.

(21) For instance, C. C. Price, *et al.*, ref. 6 and 22; J. Vaughan, *et al.*, ref. 19 and 31; P. R. Wells and E. R. Ward, ref. 9; see also E. Baciocchi, G. Illuminati and G. Marino, THIS JOURNAL, **80**, 2270 (1958).

(22) C. C. Price and R. H. Michel, *ibid.*, **74**, 3652 (1952); C. C. Price, E. C. Mertz and J. Wilson, *ibid.*, **76**, 5131 (1954).

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

(24) We are glad to acknowledge valuable conversations on this point with Dr. Frances Berliner.

(25) For yet another way of expressing substituent constants in naphthalene, see H. H. Jaffé, THIS JOURNAL, **76**, 4261 (1954).

(26) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Ch. VII; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

TABLE II

SUBSTITUENT CONSTANTS FOR THE NITRO GROUP IN NAPHTHALENE DERIVATIVES

Reaction	pK_a of acids[d]	pK_a of amines[8]	pK_a of naphthols[10]	pK_a of acids[6]	pK_a of acids[6,22]	Hydrolysis of esters[22]	Hydrolysis of esters[19,f]	Hydrolysis of acetnaphthalides[12]
Solvent	50% butyl Cellosolve	Water	48% ethanol	Water	78.1% ethanol	70% dioxane	85% ethanol	Methanol
-log k_0[a]	5.89	4.557	10.92[10]	4.203	6.37[6,22]	2.465[22,e]	3.217	6.199[12,g]
ρ[b]	1.390	2.767	2.545	1.00	2.07[6,22]	2.313	2.537	2.151
Position[c]								
1,2	1.39	2.22					−0.494	1.12
1,3	0.640	0.845					.471	0.613
1,4	1.02	1.45	1.79		0.768	0.490	.500	1.99
1,5	0.676	0.635	0.656		0.555	0.312	.332	0.388
1,6	.532	.509	0.519				.329	
1,7	.353	.624						
1,8	.460	.639					− .995	
2,1	.978	2.01						2.21
2,3		0.588						1.19
2,4	.662	.696						
2,5	.482	.505				0.416		0.214
2,6	.590	.653						.593
2,7	.504	.516						.214
2,8	.187	.613				0.331		.531
1-Naphthyl	.00	.230	0.106	0.508	0.116	− .185	− .158	− .029
(2,3-$(CH)_4$)					.217[h]		− .044[i]	
2-Naphthyl								
(3,4-$(CH)_4$)	−0.043	0.162[k]		0.042[l]	.193[h]	.00	.084[i]	− .005

[a,b] Except where otherwise indicated, these constants were taken from ref. 26b. Rate constants are in reciprocal seconds. [c] The first number indicates the position of the functional group at which reaction takes place, the second the position of the substituent. [d] Present investigation. [e] The constants from ref. 22 were taken ($n = 3$), rather than those from ref. 26b ($n = 4$), because the latter include 2-naphthyl as one of the substituents. [f] The σ-constants are based on rate constants which were recalculated to 25° using the data reported in ref. 19. [g] Because the data do not fit the Hammett Equation with the usual precision (ref. 26b, footnote 15), the experimental value for log k_0 was used rather than the calculated one. [h] A log K_0 of −6.70 was used in this calculation; see ref. 6. [i] From rate constants which were extrapolated to 25° from the data in ref. 31. By the same procedure identical σ-values had been calculated previously by S. Oae and C. C. Price, ref. 6. [k] log K for the unsubstituted naphthylamines from ref. 32. This value corresponds to the σ of 0.17 given in the original list, ref. 26. Constants of 0.022 and −0.03 have been calculated for 3,4-$(CH)_4$ from the basicities of pyridines and pyridine 1-oxides, respectively; see ref. 33. [l] This is the value suggested for 3,4-$(CH)_4$ in the recent compilation in ref. 23.

shown to hold.[26b] This constant factor will be the same in one reaction series, but will vary from reaction to reaction.

In Table II are listed the σ-values for nitro groups in naphthalene derivatives. A ρ-value of 1.390 was used for the ionization of benzoic acids in 50% by volume aqueous butyl Cellosolve.[27] The reaction to which this ρ refers was carried out in the presence of 0.05 M LiCl. This is not expected to alter ρ, although it lowers the individual pK's by about 0.2 to 0.3 pK unit. Therefore the value found for benzoic acid in the absence of LiCl was used for log K_0. Included in the table are also some data calculated from the literature, similar to the recent compilation of Wells and Ward.[28] Our data agree with those calculated by Price *et al.*, but differ from others for the reasons given above. The column headings contain the values log k_0 and ρ, which were used in the calculations.

The agreement among the values for the same substituents is not very good, although it is perhaps not worse than the precision of substituent constants for benzene derivatives, as given by their upper and lower limits.[29] It is very likely that better average values will emerge as more experimental data will become available. The agreement among the values is quite reasonable if only data derived from dissociation constants are compared, for instance the 1,5-, 1,6-, 2,4-, 2,5- or 2,7-values, but it becomes worse where steric or chelation effects might enter, such as with substituents in the 8-position. Agreement between the *ortho* compounds could not have been expected, and these values are only listed for the sake of completeness. As mentioned, values derived from 1-naphthoate hydrolysis are uniformly lower than those derived from pK's, resulting in some cases even in negative constants. For positions where strong interaction occurs (1,4), the values derived from amines and naphthols are considerably larger than those from acids, and may ultimately require a different set of values,[30] just as in the benzene series, but this does not seem to be necessary for less strongly conjugated positions (1,5, 2,6). Because of the varying steric effect, values for 1-naphthyl are very irregular, but those for 2-naphthyl cluster around the suggested value of 0.042.[23] A more detailed discussion and comparison of the various σ-values does not seem to be justified at the present time.

Experimental

Preparation of Nitronaphthoic Acids.—Of the acids, only 7-nitro-1-naphthoic acid had not been previously synthe-

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(27) Instead of the value 1.32 in ref. 4. The use of the corrected value ($n = 6$, $r = 0.99$, $s = 0.088$) does not change the σ's assigned to the *m*- and *p*-phenyl groups in ref. 23.

(28) P. R. Wells and E. R. Ward, ref. 9.

(29) Reference 26b, Table 8.

(30) This suggestion has been made before; see ref. 28 and 26b.

(31) P. Fitzgerald, J. Packer, J. Vaughan and A. F. Wilson, *J. Chem. Soc.*, 170 (1956).

(32) N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3468 (1932).

(33) H. H. Jaffé and G. O. Doak, *ibid.*, **77**, 4441 (1955).

sized. The other acids were prepared by literature procedures, except that 6-nitro- and 7-nitro-2-naphthoic acid were made from their respective nitriles as described below. Most of the acids were converted to an ester, which was then crystallized to constant melting point. The pure esters were hydrolyzed by refluxing them with a small excess of sodium hydroxide in 50% aqueous ethanol for 1.5 hours. The cooled solutions were acidified with dil. hydrochloric acid, and the acids thus obtained were crystallized one or more times from glacial acetic acid and dried to constant weight at 110°. The melting points of the acids and esters are recorded in Table III. All melting points are corrected. Those below 250° were taken on a Hershberg apparatus with total immersion thermometers; the others were taken on an aluminum block,[34] and thermometer corrections were applied. With the very high melting acids, it is not always clear if the literature values are corrected.

7-Nitro-1-naphthoic acid was prepared from 7-nitro-1-naphthylamine, which in turn was made by nitration of 1-tetralone followed by rearrangement of the oxime acetate.[35] The m.p. of the dark red 7-nitro-1-naphthylamine, obtained in 17% yield by rearrangement of the oxime acetate and in 28% yield from the oxime itself, was 130.0–130.8° after crystallization from ethanol (lit.[35] 133–134°). The amine was converted to the nitrile by the method of Hodgson and Walker.[36] The amine (1.12 g., 0.006 mole) was dissolved in 12 ml. of acetic acid and cooled with mechanical stirring. The suspension was diazotized with a solution prepared from 0.44 g. of sodium nitrite and 5 ml. of concd. sulfuric acid. At the end of the diazotization, the solution was diluted with a few drops of acetic acid and poured immediately into a well-stirred ice-cold solution prepared from 1.50 g. of $CuSO_4$ in 8 ml. of water and 14 g. of KCN in 22 ml. of water. Stirring at 8° was maintained for one hour. The reaction mixture was heated to 82° and allowed to remain at about 60° for 12 hours. Sublimation at 1 mm. and 134–145° (bath temperature) of the dried precipitate afforded fine yellow needles, which after crystallization from ethanol melted at 177–178° (0.34 g., 28.8%). A sample resublimed at 150–160° and 1.5 mm. gave fine, white needles from ethanol of m.p. 179.4–179.9°. *Anal.*[37] Calcd. for $C_{11}H_6N_2O_2$ (7-nitro-1-naphthonitrile): C, 66.66; H, 3.05. Found: C, 66.79; H, 3.12.

One gram of the nitrile was dissolved in a mixture of 40 ml. of glacial acetic acid, 20 ml. of water and 20 ml. of concd. sulfuric acid, and the mixture was refluxed for 24 hours. The cream-colored precipitate was dissolved in 100 ml. of a 5% sodium hydroxide solution, and the solution was cooled and filtered. Acidification afforded the crude acid (1.2 g.) which was immediately esterified with 60 ml. of methanol and 10 ml. of sulfuric acid. Two crystallizations from methanol of the ester yielded yellow leaflets of m.p. 175.4–176.2°. *Anal.*[37] Calcd. for $C_{12}H_9NO_4$ (methyl 7-nitro-1-naphthoate): C, 62.34; H, 3.92. Found: C, 62.35; H, 3.71. One gram of the ester was refluxed for one hour with a slight excess of sodium hydroxide and a little alcohol. The acid (1 g.), after crystallization from acetic acid (55 ml.), was obtained as yellow needles of m.p. 261.0–263.5°. *Anal.*[37] Calcd. for $C_{11}H_7NO_4$ (7-nitro-1-naphthoic acid): C, 60.83; H, 3.25. Found: C, 60.82; H, 3.40.

6-Nitro-2-naphthoic Acid.—6-Nitro-2-naphthylamine[38] was converted to the nitrile by a procedure similar to the one described above. Vacuum sublimation afforded yellow needles of m.p. 223–224° (25%) after crystallization from ethanol–acetone. Further crystallizations from ethanol and benzene, and resublimation at 0.3 mm. (150–160°) yielded mustard-yellow needles melting at 245.8–246.8°. *Anal.*[37] Calcd. for $C_{11}H_6N_2O_2$ (6-nitro-2-naphthonitrile): C, 66.66; H, 3.05. Found: C, 66.51; H, 3.01. The nitrile (1 g.) was hydrolyzed as described above, the acid was extracted with sodium hydroxide, and the crude acid (0.5 g.) melted at 314.5–325.5°. It was esterified with ethanol to give salmon-pink plates of ethyl 6-nitro-2-naphthoate of m.p. 181.1–182.3° from benzene-ligroin. Alkaline hydrolysis of the ester (1 g.) afforded the pure acid (0.7 g.) after crystallization from acetic acid.

7-Nitro-2-naphthoic Acid.[39]—The starting material for this acid, which had previously been prepared from 7-sulfo-2-naphthoic acid,[40] was naphthalic anhydride.[41] This was converted to 7-nitro-2-naphthylamine by the series of reactions described by Hodgson and co-workers.[42] The yield in the decarboxylation step could not be raised above 15%. The amine (m.p. 180–181°) was converted to the nitrile as described above. The resublimed material (24.3% after one recrystallization) was recrystallized several times from slightly aqueous ethanol and afforded pale yellow needles of m.p. 213.1–214.0°. *Anal.*[37] Calcd. for $C_{11}H_6N_2O_2$ (7-nitro-2-naphthonitrile): C, 66.66; H, 3.05. Found: C, 66.64; H, 2.89. Hydrolysis of the nitrile (42.6 mg.) with acetic acid (5 ml.), water (2.5 ml.) and sulfuric acid (2.5 ml.) afforded after one crystallization from ethanol 30 mg. (64.2%) of beige needles of 7-nitro-2-naphthoic acid. The over-all yield of pure acid, starting from naphthalic anhydride, was less than 1%.

Measurements.—Butyl Cellosolve (2-*n*-butoxyethanol, from the Union Carbide Chemicals Co.) was dried for two weeks over reagent grade calcium oxide and was then distilled through a heated Podbielniak column, a middle fraction being collected; b.p. 177–177.4° (759.3 mm.), n^{21}_D 1.4192, n^{25}_D 1.4174, sp. gr. $^{25}/_{25}$ 0.8981; lit. b.p. 170.6 (743 mm.),[43] n^{20}_D 1.41904,[44] n^{26}_D 1.4177,[43] sp. gr. $^{25}/_{25}$ 0.898.[45] The stock solution was frequently redistilled, because it decomposed slowly in the presence of trace amounts of water. The 50% volume solution contained approximately 47.2% by weight butyl Cellosolve. The dissociation constants were determined in 0.002 *M* solutions of acid by titration of the solution with a 0.05 *N* aqueous sodium hydroxide solution using a Beckman model G *p*H meter with external glass electrode and a saturated KCl–calomel reference electrode. About 18–29 mg. of acid was weighed accurately into a 250-ml. beaker which was set inside a close fitting copper container wound with copper tubing, through which water from a large thermostat was circulated. The temperature was thus kept at 25 ± 0.2°. The acid was dissolved in 25 ml. of butyl Cellosolve—heating or prolonged stirring was necessary for all heteronuclear acids—and 25 ml. of carbon dioxide free distilled water was then pipetted in. Instrument drift, particularly near the end-point of the titrations, was minimized considerably by passing nitrogen gas through a delivery tube to the bottom of the solution. The nitrogen was led through a train of four washing bottles, containing Fieser solution,[34] saturated lead acetate solution and 5% sodium hydroxide solution. Titrations were carried out with a 5-ml. micro side-arm buret graduated in hundredths. After each addition of base an exactly equivalent volume of butyl Cellosolve, saturated with nitrogen, was added to the solution from an identical buret. All operations were carefully standardized. The end-points in the titrations were determined from the inspection of the increment in *p*H per ml. of base, and the half-point acidities were then obtained graphically. The *p*H meter was standardized before and after each titration with Bureau of Standards phthalate and phosphate buffers. The error in *p*H due to uncertainty of the end-point was never greater than 0.01 *p*H unit in almost all determinations. All errors greater than 0.01 were due to changes in readings for the standard buffers during titration. Whenever that was observed, the *p*H was corrected to the average value by one-half the change. This correction was added to the error due to uncertainty in the end-point to give the errors listed in Table I. It is estimated that differences in *pK* for any two acids greater than 0.04 unit are significant. Representative results for two acids, taken over a one-

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TABLE III

NITRONAPHTHOIC ACIDS AND ESTERS[a]

Acid	M.p., °C.	Ester[b]	M.p., °C.
2-Nitro-1-naphthoic[3]	201–202 (202)[3]		
3-Nitro-1-naphthoic[41]	265.2–268.0 (270.5–271.5)[47]	Eth.	86.4–87.4 (87.5–88.5)[47]
4-Nitro-1-naphthoic[48]	224.1–224.5 (225–226)[47]	Meth.	109.2–110.3 (107.5–108.5)[47]
5-Nitro-1-naphthoic	239.2–240.9 (239)[49]	Meth.	107–108 (109–110)[49]
		Eth.	92.5–94 (92–93)[49]
6-Nitro-1-naphthoic[41]	224.9–225.3 (227–227.5)[47]	Eth.	108.9–109.9 (111.5–112)[47]
7-Nitro-1-naphthoic	261.0–263.5	Meth.	175.4–176.2
8 Nitro-1-naphthoic	215.2–217.2 (215)[49]		
1-Nitro-2-naphthoic	249.2–250.2 (239,[50] 246[51])	Meth.	146.6–147.3 (149–150)[52]
4-Nitro-2-naphthoic[53]	275–280 (270)[54]		
5-Nitro-2-naphthoic	294–295.5 (293)[55]	Eth.	108.6–109.3 (111)[55]
6-Nitro-2-naphthoic	323–325.5 (310)[40]	Eth.	181.1–182.3 (177)[40]
7-Nitro-2-naphthoic[39]	276–280 (262)[40]		
8-Nitro-2-naphthoic	292–293.5 (288)[55]	Eth.	120.5–121.1 (121)[55]
1-Naphthoic[c]	160.5–161.0 (160.5–162)[56]		
2-Naphthoic[c]	183.5–184.5 (184–185)[57]		
Benzoic[d]			

[a] All melting points are corrected. Values in parentheses are literature values. These were generally taken from those references which also describe the synthetic procedures that were followed. [b] Eth. = ethyl ester; Meth. = methyl ester. [c] A commercial sample (Distillation Products Ind.) was recrystallized twice from acetic acid, once from 95% ethanol and dried *in vacuo*. [d] The sample used in ref. 4 was used without further purification.

month interval, are: 3-nitro-1-naphthoic acid, 4.99, 5.02, 4.97, 5.00; and 8-nitro-2-naphthoic acid, 5.64, 5.63, 5.62. In the presence of 0.05 *N* lithium chloride, 5-nitro-, 6-nitro- and 7-nitro-1-naphthoic acid had values of 4.70, 4.92 and 5.12, or about 0.25 *pK* unit lower than in the absence of LiCl. Benzoic acid had *pK*'s in 0.05 *M* LiCl of 5.69 and 5.69, compared to the literature values of 5.65[4] and 5.66.[46]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Inductive Effects in Side Chain Reactions of Substituted Benzene Derivatives[1]

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Statistical methods are used for the analysis of certain aspects of an empirical relation recently proposed by Taft and Lewis for the correlation of inductive effects.

Taft and Lewis have recently proposed a new empirical relation for separating inductive effects from resonance effects in side chain reactions of substituted benzene derivatives.[2] This relation is derived on the basis of the fundamental assumption that, within a given reaction series, the resonance effect of a substituent in the *m*-position is a constant fraction of the resonance effect of the same substituent in the *p*-position. The magnitude of this constant fraction is determined by the reaction series only and is the same for all substituents in any given series. Use of this relation between the resonance effect from the *m*- and *p*-position permits the elimination of these effects (*cf.* equation 3).

$$\log k_{\mathrm{para}}/k^0 = \sigma_{\mathrm{I}}\rho_{\mathrm{I}} + R \qquad (1)$$

$$\log k_{\mathrm{meta}}/k^0 = \sigma_{\mathrm{I}}\rho_{\mathrm{I}}' + \alpha R \qquad (2)$$

$$\log k_{\mathrm{meta}}/k^0 = \alpha(\log k_{\mathrm{para}}/k^0) - \sigma_{\mathrm{I}}(\rho'_{\mathrm{I}} - \alpha\rho_{\mathrm{I}}) \qquad (3)$$

where R is the resonance effect of a substituent in the *p*-position, σ_{I} is the Taft's inductive substituent constant, ρ_{I} and ρ_{I}' are inductive reaction constants and α is the constant relating *meta* and *para* resonance effects.

Taft and Lewis made the further simplifying assumption that the value of α derived from the alkaline hydrolysis of the ethyl benzoates, $\alpha = {}^1/_3$,

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