The procedure and apparatus for utilizing the carboxylic acid as a solvent in the presence of air and steam have been described.[12]

Acknowledgment. I am indebted to Mr. R. D. Barnard, Mr. R. H. Meyer, Dr. R. W. Meikle, and Mr. A. K. Johnson for many helpful suggestions when this work was initiated.

PITTSBURG, CALIF.

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[12] W. W. Kaeding, R. O. Lindblom, and R. G. Temple, U. S. Pat. 2,727,926.

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

Resonance Interactions in Naphthalene Derivatives: Dissociation of Substituted Naphthols and Naphthoic Acids

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In order to compare resonance interactions in 4-X-1-naphthyl derivatives with those in corresponding benzene compounds, the thermodynamic *p*K values, in water at 25°, of a series of substituted 1-naphthols have been measured, together with the value for *p*-hydroxybenzophenone. An explanation has been offered for differences in resonance interaction noted for some electron-withdrawing substituents. The *p*K values, in water at 25°, of a number of substituted 1-naphthoic acids have also been determined and have been compared with those of the corresponding benzoic acids.

In recent publications Wepster and co-workers[1] and Taft and his colleagues[2,3] have shown, using different approaches, that the concept of discrete sigma values (σ^+, σ^-, and σ) is fallacious. Taft *et al.* have demonstrated that reactivity data for a select group of *meta*-substituted phenyl groups are correlated by the Hammett equation with much greater generality and precision than data for other substituted phenyl groups. They designated the mean *sigma* values, for this select group of substituents, as σ^0 values. As there is no direct conjugative interaction between *meta* substituent and side-chain reaction center (and consequently no contribution, by a resonance effect, to the relative rate) such σ^0 values are a measure of the inductive effect of an $X—C_6H_4—$ group, relative to the phenyl group. For *para*-substituted benzene derivatives, conjugation between the substituent and side-chain reaction center will occur to an extent which will vary from one reaction series to another and consequently for these substituents, a range of *sigma* values is required. Taft *et al.* obtained σ^0 values for *para*-substituted phenyl groups from the reactivities of benzyl derivatives. In these compounds resonance between the ring and reaction center is prevented by the interposed methylene group.

We have previously shown[4-6] that the Hammett reaction constant (ρ) for alkaline hydrolysis of substituted ethyl 1-naphthoates in 85% ethanol at 50° (+2.21) is not significantly different from that for the corresponding reaction of ethyl benzoates (+2.32). In ester hydrolysis, (extra) resonance contributions to the relative rates are small and insignificant, except for those *para* substituents with very large resonance (+M) effects.[7] The resonance interaction between such a substituent and the carbonyl group, which is frozen out in the transition state, is inhibited by the cross-conjugated ethoxy group. Thus the experimental result, that the relative reactivities of substituted ethyl 1-naphthoates and benzoates are closely similar, implies that the inductive effect of a substituted 1-naphthyl group (relative to the 1-naphthyl group) is equal to the inductive effect of the correspondingly substituted phenyl group (relative to the unsubstituted phenyl group). As ρ is a measure of the susceptibility of the reaction to the *inductive* effects of substituents, it follows that reaction constants for corresponding benzene and naphthalene reactions will be the same.

In order to determine whether or not resonance interactions in naphthalene derivatives, between a 4-substituent and a conjugated 1-side-chain, are the same as those in the corresponding benzene derivatives, we have measured the dissociation constants of a series of substituted 1-naphthols. The corresponding reaction in the benzene series is known to involve substantial variation in the resonance interaction between *para* −M substituted phenyl groups and side-chain, in going from reactant to product. Thus *para* −M substituted phenyl groups make a resonance contribution to

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[1] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

[2] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

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

[4] A. Fischer, J. D. Murdoch, J. Packer, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 4358 (1957).

[5] A. Fischer, J. M. Mitchell, G. S. Ogilvie, J. Packer, J. E. Packer, and J. Vaughan, *J. Chem. Soc.*, 1426 (1958).

[6] A. Fischer, H. M. Fountain, and J. Vaughan, *J. Chem. Soc.*, 1310 (1959).

[7] *Cf.* Fig. 1 and Table X of ref. 3.

the relative reactivity. We have also determined the dissociation constant of *p*-hydroxybenzophenone and, in addition, the *p*K values of several substituted 1-naphthoic acids. It was hoped that the latter would provide a second reaction series which could be used to test the conclusion that the inductive effects of correspondingly substituted 1-naphthyl and phenyl groups are equal.

EXPERIMENTAL

Physical constants of compounds examined were: *Naphthols.* 4-methyl-1-naphthol,[8] m.p. 83°; 1-naphthol, m.p. 96.5°; 4-bromo-1-naphthol,[9] m.p. 130°; 4-chloro-1-naphthol,[10] m.p. 119°; 4-hydroxy-1-naphthaldehyde,[11] m.p. 183°; 4-benzoyl-1-naphthol,[12] m.p. 165°; 4-cyano-1-naphthol,[13] m.p. 177°; 4-nitro-1-naphthol,[14] m.p. 168°; 4-nitroso-1-naphthol, m.p. 200°; 3-nitro-1-naphthol,[15] m.p. 169°; *p*-hydroxybenzophenone,[16] m.p. 135°.

Naphthoic acids. 1-naphthoic acid, m.p. 160°; 4-bromo-1-naphthoic acid,[5] m.p. 221°; 4-chloro-1-naphthoic acid,[5] m.p. 225°; 4-fluoro-1-naphthoic acid, m.p. 224.5–225°; 3-methyl-1-naphthoic acid,[5] m.p. 173.5; 3-nitro-1-naphthoic acid,[17] m.p. 269°; 4-nitro-1-naphthoic acid,[17] m.p. 225.5°. Chromatography on alumina was found to be satisfactory for purifying the small amounts of naphthols required for spectrophotometric measurements. The elution of the colorless naphthols could usually be followed by the fluorescence excited by a mercury lamp.

Thermodynamic dissociation constants were measured by the spectrophotometric method as described previously.[18] For these rather insoluble naphthalene derivatives, 4 cm. path-length cells were usually required in order to obtain optical densities in the suitable range (0.2–0.8). The temperature of the cells was maintained at 25.0 ± 0.2°. Buffers used were borax[19]; potassium dihydrogen phosphate–disodium hydrogen phosphate, pK_{HX} = 7.198[20]; 5,5′-diethylbarbituric acid (barbitone), pK_{HX} = 7.979[21]; sodium hydrogen succinate–disodium succinate[22]; formic acid–sodium formate (standard AnalaR formic acid solution partially neutralized with standard sodium hydroxide solution), pK_{HX} = 3.752[23]; potassium hydrogen tartrate, *pw*H(0.03 *m*) = 3.645[24]; chloroacetic acid–sodium chloroacetate (standard AnalaR chloroacetic acid solution partially neutralized with standard sodium hydroxide solution), pK_{HX} = 2.860.[25] For an acid HB in a buffer mixture of HX and X, pK_{HB} was obtained using one of the equations.[18]

$$pK_{HB} = pwH - \log m_B/m_{HB} - \log f_B/f_{Cl}f_{HB} \qquad (1)$$

$$pK_{HB} = pK_{HX} + \log m_X/m_{HX} - \log m_B/m_{HB} - \log f_Bf_{HX}/f_{HB}f_X \qquad (2)$$

In the case of the naphthols, with one exception, the spectrophotometric determination of m_B/m_{HB} was made at λ_{max} for the appropriate naphthoxide anion, at which wave length ϵ_{HB} was less than 2% of ϵ_B. For 3-nitro-1-naphthol the acid peak at 380 mμ was used. The optical density of some of the naphthol solutions varied slightly, depending upon the age of the solution. Moreover, certain of the solid naphthols discolored quite rapidly on standing. The naphthols were therefore always purified immediately before use and optical density measurements were made on freshly prepared solutions. The dissociation constants now reported are less precise (± 0.03) than those reported earlier for substituted phenols (± 0.01), which did not show the instability noted in the naphthol series. The naphthoxide solutions were fluorescent but the *p*K determinations were not affected by this; in each case, the solution of naphthoxide in alkali was shown to obey Beer's Law.

The naphthoic acids were found to be a much less suitable system for spectrophotometric investigation because of the small spectral change which occurs on converting the acid to anion. Thus, in the least favorable case (4-nitro-1-naphthoic acid) at the wave length used, $\epsilon_{HB}/\epsilon_B = 0.82$. For the most favorable case (1-naphthoic acid) $\epsilon_{HB}/\epsilon_B = 4.1$. These values may be contrasted with $\epsilon_{HB}/\epsilon_B < 0.02$, for the naphthols. Moreover, in the case of the naphthoic acids, the maximum difference between ϵ_{HB} and ϵ_B does not occur at λ_{max}. Consequently it was found necessary to make the spectrophotometric measurements at a steep portion of the absorption curves. For these reasons the errors in the *p*K values of the naphthoic acids are relatively large, being as high as ±0.1 unit for 4-nitro-1 naphthoic acid, and ±0.05 in the other cases.

As with the other substituted phenols,[18] the *p*K value for *p*-hydroxybenzophenone was determined with good precision (±0.01) and the mean *p*K was 7.945.

In Table I are listed the mean *p*K values of naphthols, together with the mean *p*Ks of correspondingly substituted phenols. In a similar manner, Table II contains values for the naphthoic acids, together with the relevant benzoic acids.

DISCUSSION

Naphthols and phenols. There is good agreement between our value for the *p*K of *p*-hydroxybenzophenone (7.945 ± 0.01) and that of Grunwald

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(8) L. F. Fieser and D. M. Bowen, *J. Am. Chem. Soc.*, **62**, 2103 (1940); R. E. Steiger, *Helv. Chim. Acta*, **13**, 173 (1930).

(9) W. Militzer, *J. Am. Chem. Soc.*, **60**, 256 (1938).

(10) H. Kast, *Ber.*, **44**, 1337 (1911).

(11) R. Adams and I. Levine, *J. Am. Chem. Soc.*, **45**, 2373 (1923).

(12) R. Scholl and C. Seer, *Ann.*, **394**, 111 (1912).

(13) R. T. Arnold and J. Sprung, *J. Am. Chem. Soc.*, **61**, 2475 (1939).

(14) G. N. Burkhardt and H. Wood, *J. Chem. Soc.*, 141 (1929).

(15) Sample kindly supplied by Dr. Alexander Bryson and purified (alumina column) before use.

(16) K. W. Rosenmund and W. Schnurr, *Ann.*, **650**, 89 (1928).

(17) G. J. Leuck, R. P. Perkins, and F. C. Whitmore, *J. Am. Chem. Soc.*, **51**, 1831 (1929).

(18) M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *J. Am. Chem. Soc.*, **81**, 4226 (1959).

(19) G. G. Manov, N. J. de Lollis, P. W. Lindvall, and S. F. Acree, *J. Research Natl. Bur. Standards*, **36**, 543 (1946).

(20) R. G. Bates and S. F. Acree, *J. Research Natl. Bur. Standards*, **30**, 129 (1943).

(21) G. C. Manov, K. E. Schuette, and F. S. Kirk, *J. Research Natl. Bur. Standards*, **48**, 84 (1952).

(22) G. D. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, **45**, 322 (1950).

(23) H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1042 (1934).

(24) R. G. Bates, *Chem. Rev.*, **42**, 1 (1948).

(25) D. D. Wright, *J. Am. Chem. Soc.*, **56**, 314 (1934).

(26) V. V. Perekalin, *Zhur. Obshchei Khim.*, **21**, 1057 (1951).

(27) K. Lauer, *Ber.*, **70**, 1127 (1937).

(28) P. A. Trübsbach, *Z. Physik. Chem.*, **16**, 708, 727 (1895).

(29) A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1936).

(30) A. I. Biggs and R. A. Robinson, private communication.

(31) J. M. Vandenbelt, C. Henrich, and S. G. van den Berg, *Anal. Chem.*, **26**, 726 (1954).

TABLE I

*p*K VALUES OF X-1-NAPHTHOLS AND X-PHENOLS

X	4-CH_3	H	4-Cl	4-Br	3-NO_2	4-C_6H_5CO	4-CN	4-CHO	4-NO_2	4-NO
*p*K (Naphthol)	9.64	9.39[d]	8.86	8.72	7.86	7.33	7.08	6.53	5.73	8.18[e]
Buffer[a]	I	I	I	I	III	II	II	II	IV	II
n[b]	7	3	5	3	4	4	4	4	3	3
*p*K (Phenol)	10.26[29]	9.99[18]	9.42[30]	9.36[30]	8.40[29]	7.95	7.97[18]	7.41[31]	7.15[18]	6.36[18]
Δ[c]	0.62	0.60	0.56	0.64	0.54	0.62	0.89	0.88	1.42	−1.82

[a] Buffers: I = borax; II = phosphate; III = barbitone; IV = succinate. [b] *n* = the number of *p*K′ values determined. [c] Δ = *p*K (X-phenol) − *p*K (X-naphthol). [d] Lit. values 9.60[26]; 9.85[27] (20°). [e] Lit value 6.59.[28]

TABLE II

*p*K VALUES OF X-1-NAPHTHOIC AND X-BENZOIC ACIDS

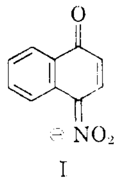
X	H	4-Br	4-Cl	4-OMe	4-F	3-CH_3	3-NO_2	4-NO_2
*p*K (naphthoic acids)	3.64[d]	3.37	3.36	4.31	3.70	3.72	2.83	2.8
Buffer[a]	I	II	II	I	I	I	III	III
n[b]	2	1	1	3	3	3	2	3
*p*K (benzoic acids)	4.20[33]	4.97[34]	4.97[34]	4.47[35]	4.14[34]	4.27[36]	3.49[36]	3.42[36]
Δ[c]	0.56	0.60	0.61	0.16	0.44	0.55	0.66	0.62

[a] I = formic acid; II = tartrate; III = chloroacetic acid. [b] *n* = the number of *p*K′ values determined. [c] Δ = *p*K (X-benzoic acid)-*p*K (X-1-naphthoic acid). [d] Lit. value 3.69.[32]

(7.98 ± 0.04)[37] obtained by a potentiometric method. On the other hand, there is surprisingly poor agreement between our value for the *p*K of 1-naphthol and those of Perekalin[26] (by potentiometric titration) and of Lauer[27] (by an indicator method). Their values were obtained by less accurate methods. Moreover, there is a good linear relationship between our *p*K values of naphthols not containing −M substituents in the 4-position and the accurate *p*K values of the corresponding phenols determined by Biggs and Robinson (see below). We therefore believe that our value is the more reliable. There is a very much larger discrepancy between the *p*K value now reported for 4-nitroso-1-naphthol, and that determined by Trübsbach.[28] There is, however, some doubt as to the exact identity of the nitrosonaphthols used by Trübsbach.[38] Within the limits of experimental error our value for the *p*K of 1-naphthoic acid agrees with the presumably more accurate value of Dippy *et al.*[32]

When the *p*K values of substituted 1-naphthols are plotted against *p*K's of the corresponding phenols, it is found that substituents incapable of resonance interaction with the side-chain correlate well with a line drawn on the assumption that reaction constants, for the dissociation of phenols and 1-naphthols, are the same. On the other hand, when resonance interaction exists, the relevant points (with the exception of that for the 4-benzoyl substituent) are well off the line. The points for the 4-CN, 4-CHO, and 4-NO_2 substituents indicate greater acidity, of the respective naphthols, than would be implied by the linear relationship, and the point for the 4-NO group indicates that the acidity of the corresponding naphthol is lower than would be expected.

Consider first the data for the compounds in which the 4-substituent is CN, CHO, or NO_2. The fact that these substituted 1-naphthols are stronger acids than the linear correlation indicates that there is (relative to the unsubstituted compound) a greater gain in resonance energy in ionization of such a substituted naphthol than there is in the case of the corresponding phenol. This appears to be reasonable; two singly-charged canonical structures can be written for the quinoid form of,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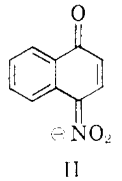
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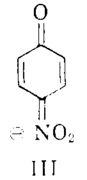
III

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

(33) J. Packer, J. Vaughan, and E. Wong, *J. Org. Chem.*, **23**, 1373 (1958).

(34) J. F. J. Dippy, F. R. Williams, and R. H. Lewis, *J. Chem. Soc.*, 343 (1935).

(35) J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 1888 (1934).

(36) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 644 (1936).

(37) E. Grunwald, *J. Am. Chem. Soc.*, **73**, 4934 (1951).

(38) Elsevier's *Encyclopaedia of Organic Chemistry*, Elsevier Publishing Co., Amsterdam, 1952, Vol. 12B, p. 2731, footnote.

e.g., 4-nitro-1-naphthoxide ion (I & II), but only one for the 4-nitro-phenoxide ion (III). Expressed another way, the greater resonance interaction between 4-substituent and 1-side-chain in the naphthalene case is a result of the "naphthoquinone type" structure containing a benzene ring. As the resonance energy difference between naphthalene and benzene is less than the resonance energy of benzene, the "naphthoquinone type" structure contributes more to the resonance hybrid of naphthoxide and "quinone type" forms than the "benzoquinone type" does to the resonance hybrid in the corresponding benzene case.

For 4-benzoyl-1-naphthol, models show that the carbonyl group cannot achieve coplanarity with the naphthalene ring because of the steric effect of the adjacent *peri* hydrogen atom. In this instance it appears that the effect of steric hindrance to mesomerism just balances the additional resonance effect expected for a naphthalene derivative. Some steric hindrance is similarly expected in 4-nitro-1-naphthol, but in this case it is insufficient to outweigh the additional naphthalene resonance effect. The apparent paradox, that 4-nitroso-1-naphthol is a much weaker acid than *p*-nitrosophenol, may also be explained in terms of the "naphthoquinone type" structure being relatively more stable than the "benzoquinone type" structure.[39] 4-Nitroso-1-naphthol and *p*-nitrosophenol are both tautomeric and in solution we have the equilibria (charges not shown)

$$\underset{\text{nitroso}}{\mathrm{HB}} \overset{\mathrm{K_I}}{\rightleftharpoons} \mathrm{H} + \underset{\text{anion}}{\mathrm{B}} \rightleftharpoons \underset{\text{quinone monoxime}}{\mathrm{HB'}}$$

It may be shown that the measured equilibrium constant is

$$\mathrm{K_{exptl}} = (\mathrm{a_{H}a_{B}})/(\mathrm{a_{HB}} + \mathrm{a_{HB'}}) = \alpha(\mathrm{a_{H}a_{B}}/\mathrm{a_{HB}}) = \alpha\mathrm{K_I}$$

where α is the fraction of the compound in the nitroso form. Denote naphthol case by superscript N and phenol by P. Then

$$p\mathrm{K^P}_{\mathrm{exptl}} = -\log \alpha^{\mathrm{P}} + p\mathrm{K^P}_1$$

$$p\mathrm{K^N}_{\mathrm{exptl}} = -\log \alpha^{\mathrm{N}} + p\mathrm{K^N}_1$$

If, as for other 1-naphthols and phenols with $-$M 4-substituents

$$p\mathrm{K^N}_1 \ngtr p\mathrm{K^P}_1$$

then

$$\log \alpha^{\mathrm{N}} + p\mathrm{K^N}_{\mathrm{exptl}} \ngtr \log \alpha^{\mathrm{P}} + p\mathrm{K^P}_{\mathrm{exptl}}$$

hence

$$\log \alpha^{\mathrm{N}} - \log \alpha^{\mathrm{P}} \ngtr -1.82$$

and

$$\alpha^{\mathrm{N}}/\alpha^{\mathrm{P}} \ngtr 0.015$$

Thus, in aqueous solution, even if all the nitrosophenol is present as the nitroso tautomer, effectively all of the nitroso-naphthol exists in the quinonemonoxime form—i.e. the "naphthoquinone type" tautomer is relatively more stable than the "benzoquinone type" tautomer.

The mesomeric interaction energy differences ($\simeq\Delta\mathrm{E}_\psi$)[3] for the 4—CN—, 4—CHO—, and 4—NO$_2$— substituted 1-naphthols and phenols have been calculated from the expression

$$\Delta\Delta\mathrm{F}_\psi{}^{\pm} = 2.3\mathrm{RT}(p\mathrm{K} - p\mathrm{K}^0 + \rho\sigma^0)$$

These are listed in Table III. As no σ^0 value is available for the *p*-cyanophenyl or *p*-formylphenyl groups, the *sigma* value from benzoic acid dissociation is used for the former and that of *p*-acetylphenyl, again from benzoic acid dissociation, for the latter.[40]

TABLE III

$\Delta\Delta\mathrm{F}_\psi$ VALUES (Kcal. Mole^{-1}) FOR DISSOCIATION OF X-1-NAPHTHOLS AND X-PHENOLS

X	4-CN	4-CHO	4-NO$_2$
$-\Delta\Delta\mathrm{F}_\psi$ (Naphthols)	1.1	2.3	2.5
$-\Delta\Delta\mathrm{F}_\psi$ (Phenols)	0.7	1.9	1.4

Consider now the data for those compounds which do not involve resonance interaction between substituent and side-chain. From Table III it is seen that these substituted 1-naphthols are, on the average, more acid than the correspondingly substituted phenols by 0.59 *p*K units. It has previously been shown that the polar effect of a 1-naphthyl substituent (relative to phenyl) is very small ($\sigma^* = -0.026$).[33] Consequently nonpolar factors must be responsible for the greater acidity of these naphthols. The nonpolar contribution to the relative *p*K values is

$$\mathrm{E_S} = p\mathrm{K^P} - p\mathrm{K^N} - \rho\sigma^* = 0.65$$

Furthermore, the steric effect (presumably steric inhibition of solvation of the naphthoxide ion) should be negative—*i.e.*, should result in the 1-naphthols being weaker acids than the phenols. Hence, the greater acidity of the naphthols must be attributed to a resonance effect of the 1-naphthyl group, and this must be given by

$$\Delta\Delta\mathrm{F}_\psi \ngtr -2.3\mathrm{RTE_S}$$

$$\ngtr -0.89\text{k.cal.mole}^{-1}$$

Thus the 1-naphthyl group has an "extra resonance" ($-$M) effect greater than that of the *p*-cyanophenyl group (Table III).

Carboxylic acids. Neglecting the values for the 4-methoxy and 4-fluoro substituents, the mean Δ value is 0.60 and the individual values do not deviate from this mean by more than the experimental error—*i.e.*, the reaction constants for

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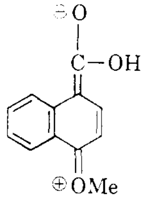
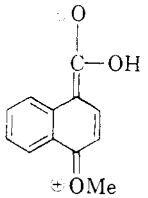
[39] A helpful note by a referee has referred us to other evidence, indicating the greater stabilization of naphthoquinone than benzoquinone, obtained from studies on hydroxy azo compounds, *e.g.*, P. Ramart-Lucas, M. Grumez, and M. Martynoff, *Bull. soc. chim.*, **10**, 233 (1943).

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

dissociation of benzoic and of 1-naphthoic acid are the same. The fact that the 4-fluoro and, particularly, the 4-methoxy-1-naphthoic acids are relatively weaker than the linear relation would predict, as shown by the low Δ values, is indicative of a greater resonance interaction in these 1-naphthoic acids, containing substituents with large +M effects, than in the corresponding benzoic acids—*i.e.*, as in the case of the 4(−M)-substituted 1-naphthoxide ions, the "naphthoquinone type" structures (IV) and (V) contribute more to the resonance hybrid of the acid than the "benzoquinone type" does in the benzoic acid case (VI).



IV



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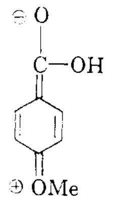

VI

However, because of the rather large experimental uncertainty of the dissociation constants of substituted 1-naphthoic acids, these conclusions are drawn with some diffidence. As in the case of the naphthols and phenols, nonpolar effects must be responsible for the greater acidity of the substituted 1-naphthoic acids compared with the correspondingly substituted benzoic acids. In this case, however, the dominant effect must be steric inhibition of mesomerism because in the absence of this factor the 1-naphthyl group, with a presumed greater +M effect than phenyl, should stabilize the acid relative to the anion and consequently inhibit dissociation.

Acknowledgment. The authors are indebted to the Research Fund Committee, of the University of New Zealand, for financial assistance.

CHRISTCHURCH, NEW ZEALAND

[CONTRIBUTION FROM THE JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Structure and Properties of Benzonaphthofurandione Derivatives

MARIO F. SARTORI

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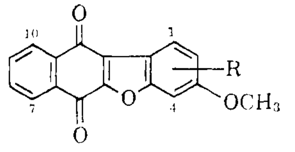
Nitration of 3-methoxybenzo[*b*]naphtho[2,3-*d*]furan-6,11-dione (I) gives derivatives with nitro groups in the benzene ring. Derivatives with a nitro group in the naphthalene system could not be obtained by direct nitration and were prepared by condensing 2,3-dichloro-5-nitro-1,4-naphthoquinone with 3-methoxyphenol. Several nitro- and aminomethoxybenzonaphthofurandiones are described and their spectral characteristics discussed. The 7- and 10-substituted benzonaphthofurandiones are useful as dyes.

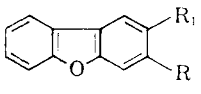
The object of this study has been to investigate the structure and the properties of nitro and amino derivatives of 3-methoxybenzo[*b*]naphtho[2,3-*d*]furan-6,11-dione (I).[1,2]



I. R = H
II. R = 2-NO_2
III. R = 2-NH_2
IV. R = 2,4-$(NO_2)_2$
V. R = 2,4-$(NH_2)_2$

The interest in these compounds lies in their attractive properties as dye-intermediates and as dyes for synthetic fibers. The present paper reports that the nitration of I yields the 2-nitro (II) and the 2,4-dinitro derivatives (IV). The 7-nitro (VII) and the 10-nitro isomer (XI) could not be prepared by direct nitration and are obtained by condensing 2,3-dichloro-5-nitro-1,4-naphthoquinone with 3-methoxyphenol.

Nitration of I in sulfuric acid with one equivalent of nitric acid gave a 70% yield of a mononitro derivative, which by oxidative degradation with potassium permanganate gave nitro-free phthalic acid, thus demonstrating that the nitro group is not in the naphthalene system. (Under the same conditions the 7-nitro derivative (VII) gave 3-nitrophthalic acid). Analogy with the structurally related dibenzofurans (VI), obtained by electrophilic substitution reactions,[3,4] suggested structure II.



VI

R = —OCH_3, —NH_2, —$NHCOCH_3$, etc.
R_1 = —NO_2, —Br, etc.

Evidence to support this structure is provided by the spectral characteristics. The nitro group in

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(1) St. v. Kostanecki and V. Lampe, *Ber.*, **41**, 2375 (1908).

(2) J. N. Chatterjea, *J. Indian Chem. Soc.*, **31**, 101 (1954).

(3) H. Gilman, G. E. Brown, W. G. Bywater, and W. H. Kirkpatrick, *J. Am. Chem. Soc.*, **56**, 2473 (1934).

(4) P. R. Van Ess, *Iowa State Coll. J. Sci.*, **12**, 164 (1937).