mesomeric effect. (Here M_i will include a contribution from the π-inductive effect; see above.) The transmission coefficient τ_{ij} can be estimated in two ways. First, it can be shown[13] that where π_{ij} is the atom-atom polarizability[14] of atoms i, j

$$\tau_{ij} \sim \pi_{ij} \qquad (3)$$

Secondly, since τ_{ij} is independent of the substituent, it can be estimated by taking one particular case. If the substituent is $-CH_2^-$, the formal negative charge (δq_{ij}) at atom j will be proportional to τ_{ij}. In the case of alternant hydrocarbons

$$\delta q_{ij} = a^2_{oj} \qquad (4)$$

where a_{oj} is the coefficient in the non-bonding molecular orbital of the ion $ArCH_2^-$ at atom j,[15] the methylene group being attached at atom i. These coefficients can be determined very simply.[15]

(e) The transmission of the electromeric effect can be shown to be proportional in a first approximation to that of the mesomeric effect,[16] *i.e.*, proportional to π_{ij} or a^2_{oj}.

The variation of each effect with distance can thus be estimated, at least to a first approximation. However, the absolute importance of the various effects in any given case cannot be estimated theoretically. It is therefore essential to have extensive data for the effects of substituents in a variety of ring systems, the substituents being at varying distances from a reaction center. Data of this kind have been lacking.

Although several hundred series of benzene derivatives have been studied, involving a great variety of substituents and reactions, no systematic investigation has been reported for any other system. Without data of this kind it is impossible to make further progress, given the inadequacy of present chemical theory. Almost the only studies of this kind reported have been those of Berliner and Blommers on the effects of 3′- and 4′-substituents on biphenyl-4-carboxylic acid,[17] of Berliner and Liu[18] on the rates of hydrolysis of the corresponding ethyl esters, of Berliner and Winicov[19] on the dissociation constants of the nitronaphthoic acids, of Fischer, Mitchell, Ogilvie, Packer, Packer and Vaughan[20] on the rates of hydrolysis of substituted ethyl 1-naphthoates, and of Bryson[21] on the effects of substituents on the basicities of 1- and 2-naphthylamines. None of these investigations covered a sufficient range of substituents to be useful.

We have accordingly synthesized a large variety of substituted 1-naphthoic acids, carrying substituents in all five unhindered positions, and have studied the effects of the substituents on the acid strength and on the infrared carbonyl frequencies of the corresponding methyl esters. This work, and the conclusions drawn from it, are described in the following papers.

P.J.G. gratefully acknowledges the award of a maintenance grant by the Department of Scientific and Industrial Research.

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[13] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3350, 3356 (1952); *cf.* theorems 34, 35, 36, 71, 72.

[14] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **A192**, 16 (1947).

[15] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

[16] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3350 (1950); *cf.* theorems.

[17] E. Berliner and E. A. Blommers, *J. Am. Chem. Soc.*, **73**, 2479 (1951).

[18] E. Berliner and L. H. Liu, *ibid.*, **75**, 2417 (1953).

[19] E. Berliner and E. H. Winicov, *ibid.*, **81**, 1639 (1959).

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

[21] A. Bryson, *J. Am. Chem. Soc.*, **82**, 4862 (1960).

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

Substituent Effects. II.[1a] The Preparation of a Series of Substituted 1-Naphthoic Acids

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The physical properties of thirty-three 1-naphthoic acids and their methyl esters are reviewed. The preparations of several new disubstituted naphthalenes and of known disubstituted naphthalenes by new routes are described.

This paper describes the syntheses and physical properties of thirty-three 1-naphthoic acids and their derivatives which were prepared for the reasons indicated in Part I. Seven of the acids have not been described previously, while a number of the others have been prepared by improved routes. The methods of synthesis are indicated below; new reactions and new compounds are indicated by asterisks. References (in parentheses) are given to reactions previously described. The melting points of the acids are listed in Table I together with literature values where available.

The syntheses followed conventional routes and only a few points need comment. (a) The replacement of Br by CN by the action of cuprous cyanide in dimethylformamide gave excellent yields.[2a] (b) Hydrolysis of the cyanonaphthoic esters to cyanonaphthoic acids required carefully controlled conditions when the cyano group occupied a β-position. (c) Repeated attempts to reduce the formyl group to methyl in methyl 3-formyl-1-naphthoate failed, using the Huang-Minlon method or catalytic reduction.[2b] We had

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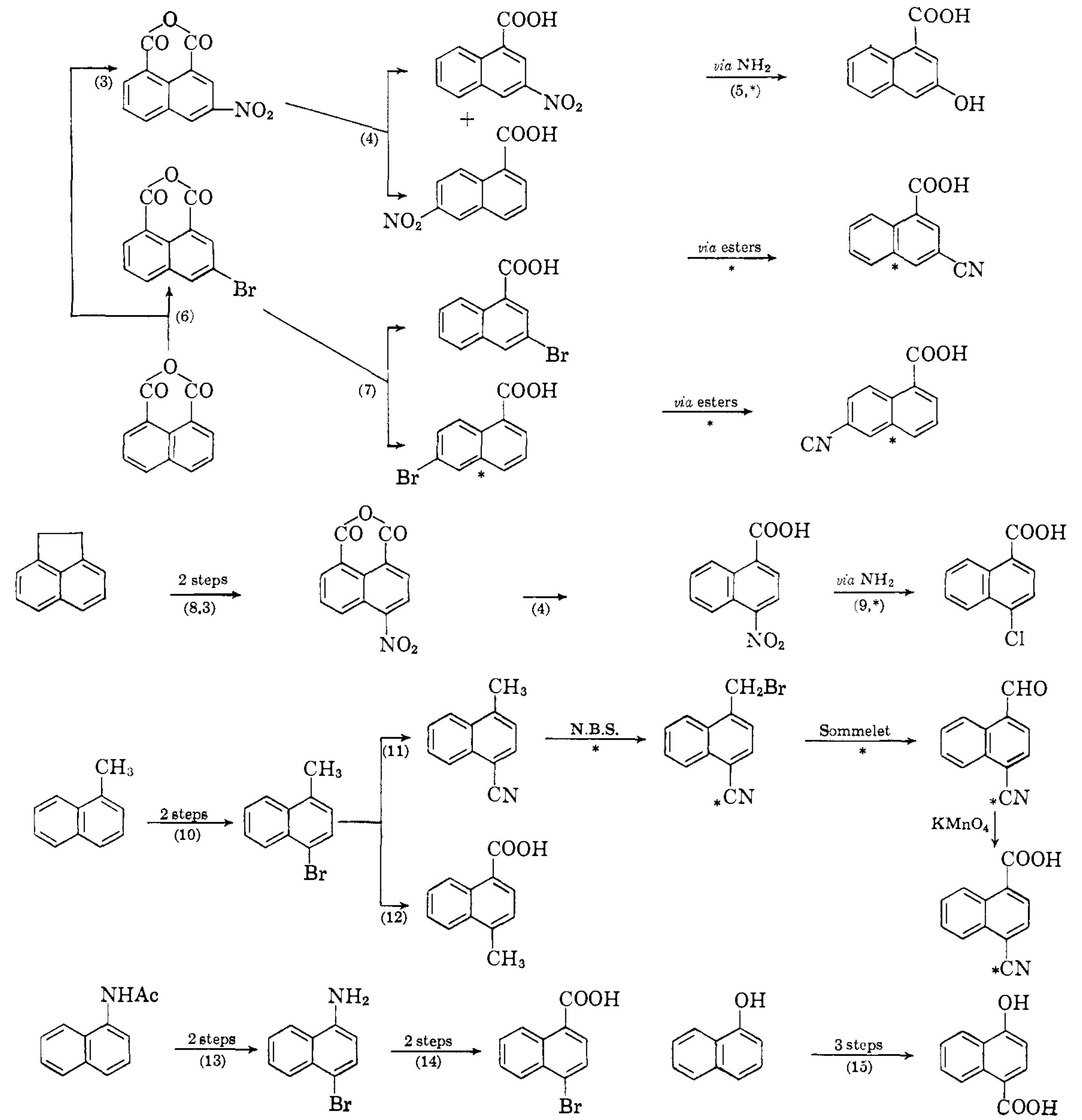
[1a] Part I, *J. Am. Chem. Soc.*, **84**, 3539 (1962).

[1b] George Herbert Jones Laboratory, University of Chicago, Chicago 37, Ill.

[2a] L. Friedman and H. Schechter, *J. Org. Chem.* **26**, 2522 (1961).

[2b] N. P. Buu-Hoi and D. Lavit, *ibid.*, **22**, 912 (1957); R. Robinson and F. Weygand, *J. Chem. Soc.*, 386 (1941).



hoped in this way to obtain 3-methyl-1-naphthoic acid. (d) 6-Bromo-1-naphthoic acid does not seem to have been isolated previously from the product obtained by mercuration of 3-bromonaphthalic anhydride and then treatment with acid,[7] although 3-methoxy- and 3-nitronaphthalic anhydrides give mixtures of 3- and 6-methoxy or nitro-1-naphthoic acids under these conditions.[4,15a]

We obtained a small yield of 6-bromo-1-naphthoic acid, identical with a sample synthesized by an unambiguous route.

Experimental

Melting points are uncorrected. Microanalyses were carried out by Alfred Bernhardt, Max-Planck-Institut, Mulheim, Germany. Chromatography was carried out with Peter Spence alumina type H, 100/200 mesh.

3-Hydroxy-1-naphthoic Acid.[6]—The sulfate of 3-amino-1-naphthoic acid (6 g.) was dissolved in dilute ammonium hydroxide (20 ml., 2 *N*) and reprecipitated in a fine state by the addition of dilute sulfuric acid (40 ml., 2 *N*). This suspension was cooled to room temperature, diazotized with a solution of sodium nitrite (1.8 g.) in water (20 ml.), and the solution run dropwise into boiling dilute sulfuric acid (2 l., 2 *N*) during 6 hours. Too rapid addition or too dilute acid resulted in the formation of a red dye. The hot solution was treated with charcoal, filtered, cooled, and extracted with ether. The crude acid was extracted from the ethereal

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(3) C. Graebe, *Ann.*, **327**, 84 (1903).

(4) G. J. Leuck, R. P. Perkins and F. C. Whitmore, *J. Am. Chem. Soc.*, **51**, 1833 (1929).

(5) R. G. Gould and W. A. Jacobs, *J. Biol. Chem.*, **130**, 141 (1937).

(6) H. G. Rule and S. B. Thomson, *J. Chem. Soc.*, 1764 (1937).

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(11) H. G. Rule, N. Campbell, A. G. McGregor and A. A. Woodham, *J. Chem. Soc.*, 1816 (1950).

(12) F. Mayer and A. Sieglitz, *Ber.*, **55**, 1835 (1922).

(13) H. H. Hodgson and S. Birtwell, *J. Chem. Soc.*, 321 (1943).

(14) F. F. Blicke and M. Gomberg, *J. Am. Chem. Soc.*, **45**, 1765 (1923).

(15) J. Houben and W. Fischer, *Ber.*, **60**, 1759 (1927).

(15a) K. Dziewonski and W. Kahl, *Bull. Intern. Acad. Polon. A*, 394 (1934).

TABLE I

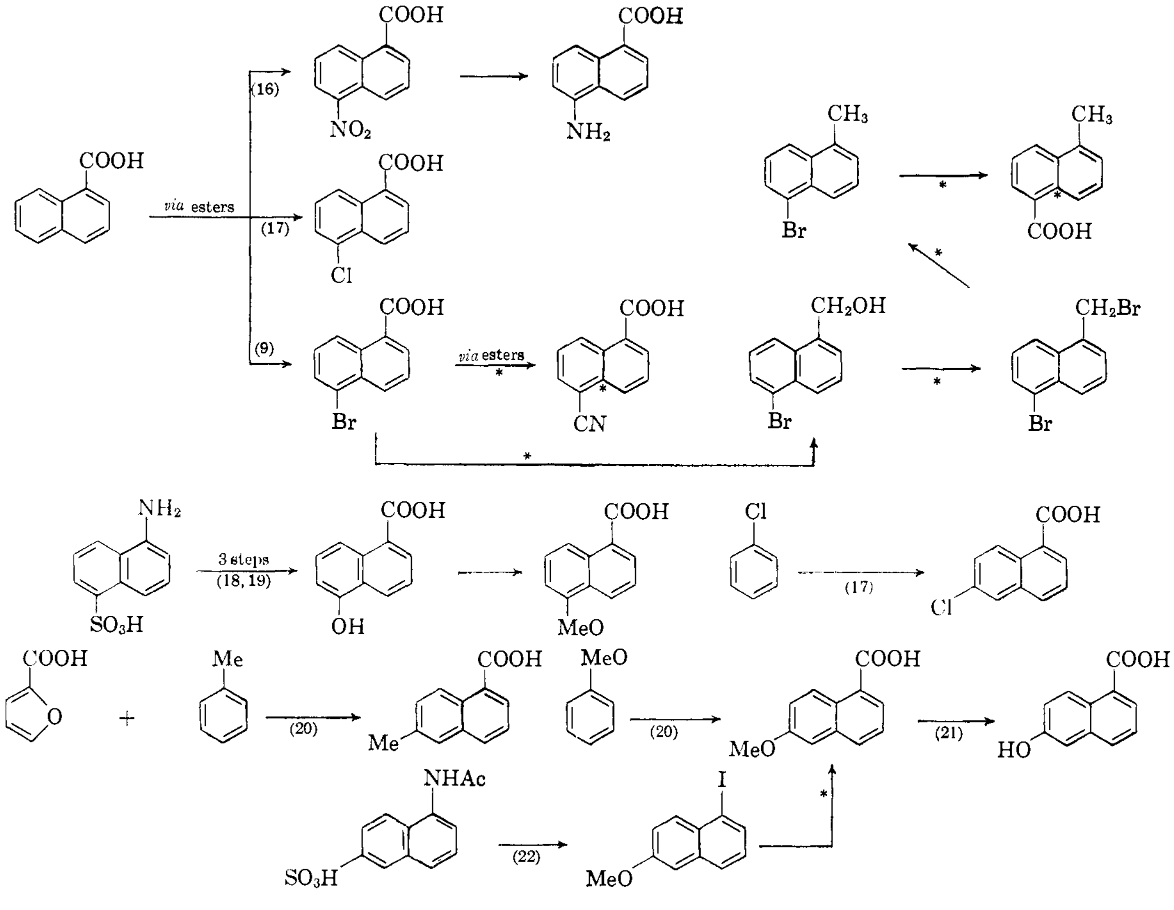
MELTING POINTS, °C., OF SUBSTITUTED 1-NAPHTHOIC ACIDS $X\text{-}C_{10}H_6CO_2H$[a]

Substituent	3-*x*	4-*x*	5-*x*	6-*x*	7
NO_2	266-268	224-225.5	242-243	225-225.5	266.5-267.5
	(265.2-268)[35]	(224.1-224.5)[35]	(239.2-240.9)[35]	(224.9-225.3)[35]	(261-263.5)[35]
CN	210	236-237	260-260.5	284-286	277-278 dec.
Cl	...	220-221	246.247	216-216.5	...
	...	(210)[32]	(245)[17]	(215.8-216.2)[17]	...
Br	233-234	219-220	258-259	185-186	235-236
	(237-238)[7]	(217-220)[14]	(256-256.5)[9]	...	(237)[27]
Me	...	176-177	188-189	178-179	146-147
	...	(175-176)[12]	...	(176.5-177)[20]	(147-148)[36]
MeO	...	240-241	230-232	179-180	166.5-167.5
	...	(243-244)[b]	(230)[33]	(180-180.5)[20]	(169-170)[26]
OH	245-246	187-188	234-235.5 d.	210-211	255-257
	(243-244)[4]	(188-189)[15]	(237-240 d.)[c]	(212.5-213)[21]	(255-256)[26]
NH_2	...	193-194	186 d.	...	...
		(176)	(1 mole H_2O)	...	...

[a] Literature values in parentheses. [b] L. F. Fieser and V. Desreux, *J. Am. Chem. Soc.*, 60, 2255 (1938). [c] J. Cason, *ibid.*, **63**, 828 (1941).

layer and recovered by acidification. Crystallization from water gave pure 3-hydroxy-1-naphthoic acid as yellow needles, m.p. 245-246° (lit.[4] 243-244°).

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.2; H, 4.3. Found: C, 70.5; H, 4.3.



Methyl 3-Cyano-1-naphthoate.—A solution of methyl 3-bromo-1-naphthoate[7] (2.65 g.) and cuprous cyanide (0.9 g.) in dimethylformamide (20 ml.) containing pyridine (2 drops) was heated at 180° for 5 hours. This hot solution was poured into ammonium hydroxide solution (50 ml., d. 0.880) containing crushed ice (50 g.). The resulting suspension was extracted with chloroform (2 × 100 ml.), washed with dilute hydrochloric acid and water, and dried ($MgSO_4$). Evaporation gave crude methyl 3-cyano-1-naphthoate, which was purified by chromatography from chloroform-petroleum ether (1:1) on alumina. The ester (1.08 g.,

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(16) H. G. Rule and A. J. G. Barnett, *J. Chem. Soc.*, 175 (1932).

(17) T. L. Jacobs, S. Winstein, *et al.*, *J. Org. Chem.*, **11**, 229 (1946).

(18) F. A. Royle and J. A. Schedler, *J. Chem. Soc.*, 1641 (1923).

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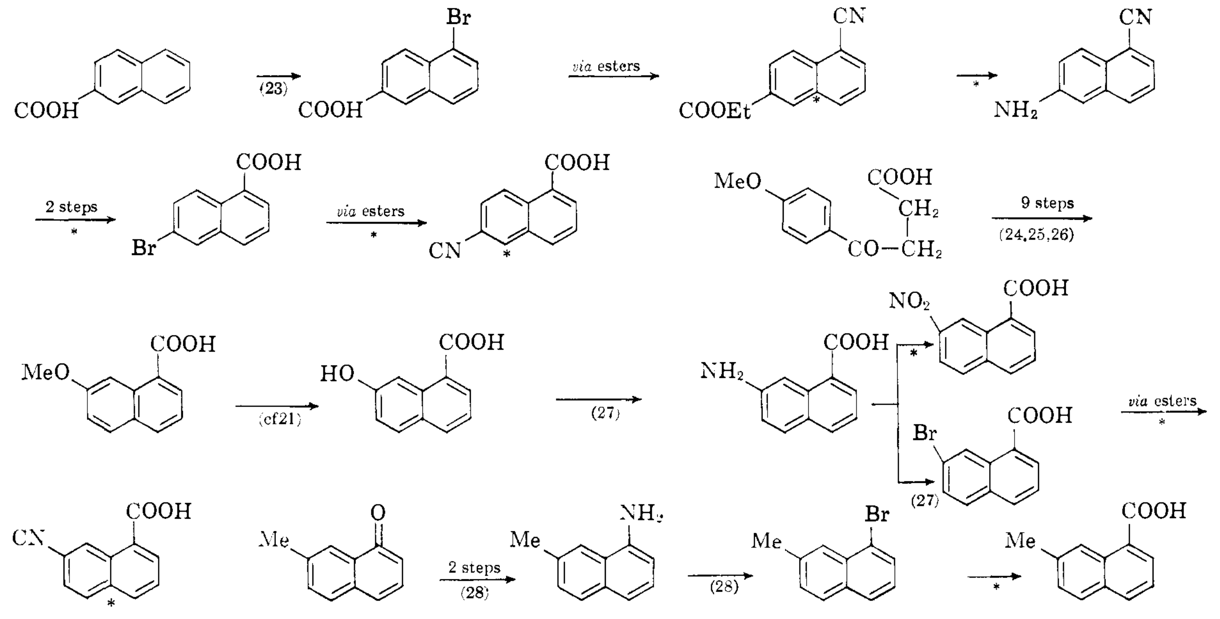
(21) L. Long and S. Burger, *J. Org. Chem.*, **6**, 852 (1941).

(22) A. Butenandt and G. Schramm, *Ber.*, **68**, 2087 (1936).



51%) crystallized from petroleum ether (b.p. 60–80°) in fine white needles, m.p. 107.5–108.5°.

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.9; H, 4.3; N, 6.6. Found: C, 73.5; H, 4.0; N, 6.6.

3-Cyano-1-naphthoic Acid.—Methyl 3-cyano-1-naphthoate (0.5 g.) in ethanol (20 ml.) was treated with sodium hydroxide solution (2.0 ml., *N*; 2.37 ml. is required for total saponification of the ester group). Chloroform (5 ml.) was added to dissolve the ester, and the solution left overnight at 40°. Water (50 ml.) was added and the solution extracted with chloroform (2 × 25 ml.). Acidification of the aqueous layer yielded 3-cyano-1-naphthoic acid (0.32 g.). It crystallized from dilute ethanol in white needles, m.p. 210–212°.

Anal. Calcd. for $C_{12}H_7NO_2$: C, 73.1; H, 3.6; N, 7.1. Found: C, 73.1; H, 3.6; N, 7.2.

Methyl 3-Formyl-1-naphthoate.—Methyl 3-cyano-1-naphthoate (2.02 g.) was dissolved in dry ether (20 ml.) and dry tetrahydrofuran (10 ml.) and added to a slurry of anhydrous stannous chloride (4 g.) in dry ether (20 ml.) saturated with hydrogen chloride. Hydrogen chloride was passed through the solution for one hour and the mixture left overnight. The precipitated aldimine hydrochloride was filtered, washed with ether, and decomposed with water. The crude formyl compound (1.61 g. 72%) was recrystallized from light petroleum (b.p. 60–80°) giving pale yellow needles of pure **methyl 3-formyl-1-naphthoate,** m.p. 104–105°.

Anal. Calcd. for $C_{13}H_{10}O_3$: C, 73.0; H, 4.7. Found: C, 72.5; H, 4.6.

4-Chloro-1-naphthoic Acid.—4-Amino-1-naphthoic acid[32] was diazotized and converted to the chloro acid by the method of Goldstein and Fischer.[27] Sublimation of the crude acid at 160° (0.2 mm.) gave 4-chloro-1-naphthoic acid which crystallized from dilute methanol in fine white needles, m.p. 220–221°, lit.[29] 210°.

Anal. Calcd. for $C_{11}H_7ClO_2$: C, 63.9; H, 3.4; Cl, 17.1. Found: C, 63.8; H, 3.4; Cl, 17.1.

1-Bromomethyl-4-cyanonaphthalene.—1-Methyl-4-cyanonaphthalene[11] (10 g.) in carbon tetrachloride (60 ml.) was heated on a water-bath for 1 hour with N-bromosuccinimide (11.4 g.) and a trace of benzoyl peroxide. The hot solution was filtered, diluted with chloroform (40 ml.) and shaken with water to remove succinimide. The organic layer was dried ($MgSO_4$) and evaporated, yielding **1-bromomethyl-4-cyanonaphthalene** (14.5 g., 95%) which crystallized from ethanol in pale yellow needles, m.p. 134–135°.

Anal. Calcd. for $C_{12}H_8BrN$: C, 58.5; H, 3.3; Br, 32.5; N, 5.7. Found: C, 58.2; H, 3.3; Br, 32.6; N, 5.6.

1-Formyl-4-cyanonaphthalene.—1-Bromomethyl-4-cyanonaphthalene (3 g.) and hexamine (19 g.) were refluxed for 2 hours in chloroform (120 ml.). The hexaminium salt was refluxed for 90 minutes in acetic acid–water (1:1, 100 ml.). Concentrated hydrochloric acid (1.5 ml.) was then added and the solution refluxed for a further 5 minutes. The solution was diluted with water until just cloudy and on cooling the pure **1-formyl-4-cyanonaphthalene** came down as very pale yellow needles (1.3 g. 59%). Recrystallization from alcohol produced similar needles, m.p. 143–144°.

Anal. Calcd. for $C_{12}H_7ON$: C, 79.5; H, 3.9; N, 7.7. Found: C, 79.0; H, 4.3; N, 8.0.

4-Cyano-1-naphthoic Acid.—4-Cyano-1-formylnaphthalene (0.5 g.) in 50% v./v. aqueous acetone (20 ml.) was treated with a solution of potassium permanganate (0.6 g.) and sodium carbonate (0.1 g.). The solution was gently warmed until manganese dioxide separated, then filtered, and the acid (0.38 g., 62%) precipitated from the filtrate with a stream of sulfur dioxide. Extraction with sodium bicarbonate and recrystallization from ethanol gave white needles of **4-cyano-1-naphthoic acid.** m.p. 236–237°.

Anal. Calcd. for $C_{12}H_7NO_2$: C, 73.1; H, 3.6; N, 7.1. Found: C, 73.0; H, 3.6; N, 7.1.

Methyl 4-Cyano-1-naphthoate.—Prepared from the cyano acid and diazomethane in ether, the ester crystallized from dilute ethanol in white needles, m.p. 107–108°.

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.9; H, 4.3; N, 6.6. Found: C, 73.6; H, 4.2; N, 6.4.

5-Bromo-1-hydroxymethylnaphthalene.—Methyl 5-bromo-1-naphthoate (5.3 g.) in dry ether (30 ml.) was added slowly with stirring to lithium aluminum hydride (0.85 g.) in ether (100 ml.) at 5°. After 30 minutes, the excess lithium aluminum hydride was decomposed with moist ether and the ethereal solution washed with dilute sulfuric acid, water, dried ($MgSO_4$), and evaporated to give 5-bromo-1-hydroxymethylnaphthalene (4.1 g., 86.5%), m.p. 121–123°. A sample crystallized from benzene in white needles, m.p. 123–124° (lit.[30] 124°).

5-Bromo-1-methylnaphthalene.—5-Bromo-1-bromomethylnaphthalene (2 g.), prepared from the corresponding hydroxy methyl compound by the method of Shoesmith and Rubli[33] in dry tetrahydrofuran (50 ml.), was treated slowly with lithium aluminum hydride (0.4 g.) in dry tetra-

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(23) J. Jacques, *Bull. soc. chim. France*, 857 (1953).

(24) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(25) L. F. Fieser and E. B. Hershberg, *ibid.*, **58**, 2314 (1936).

(26) L. F. Fieser and H. L. Holmes, *ibid.*, **58**, 2319 (1936).

(27) H. Goldstein and H. A. Fischer, *Helv. Chim. Acta*, **21**, 1519 (1938).

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(29) P. Friedlaender and J. Weisberg, *Ber.*, **28**, 1838 (1895).

(30) J. B. Shoesmith and H. Rubli, *J. Chem. Soc.*, 3098 (1927).

hydrofuran (50 ml.). The solution was refluxed for 1 hour, cooled, and the excess lithium aluminum hydride decomposed with moist tetrahydrofuran. Dilute sulfuric acid (200 ml., 2 *N*) was added and the solution extracted continuously with ether for 2 hours. The dried ethereal solution was evaporated. Recrystallization of the residue from petroleum ether (b.p. 40–60°) gave 5-bromo-1-methylnaphthalene as white needles (1 g., 68%), m.p. 59–60° (lit.[31] 63–64°).

5-Methyl-1-naphthoic Acid.—The Grignard reagent from 5-bromo-1-methylnaphthalene (1 g.) in dry tetrahydrofuran (10 ml.) was poured onto solid carbon dioxide. Ether (60 ml.) and dilute sulfuric acid (30 ml., 2 *N*) were added. The organic layer was separated, washed with water and the acid extracted with sodium bicarbonate solution, which on acidification with dilute hydrochloric acid yielded 5-methyl-1-naphthoic acid (0.7 g., 83.5%), m.p. 184–186°. Recrystallization from dilute ethanol gave the pure acid in white plates, m.p. 188–189°.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.4; H, 5.4. Found: C, 77.3; H, 5.4.

Methyl 5-Methyl-1-naphthoate.—The ester obtained from the acid with diazomethane in ether crystallized from methanol–water in fine white needles, m.p. 39°.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 78.0; H, 6.0. Found: C, 77.7; H, 5.9.

Methyl 5-Cyano-1-naphthoate.—Methyl 5-bromo-1-naphthoate was converted to the cyano ester by the method described for the 3-isomer. Purification by chromatography gave **methyl 5-cyano-1-naphthoate** (72%). Two recrystallizations from petroleum ether gave white needles, m.p. 109–110°.

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.9; H, 4.3. Found: C, 74.2; H, 4.4.

5-Cyano-1-naphthoic Acid.—Obtained from the ester in quantitative yield by hydrolysis with hydrochloric acid in dilute acetic acid, the acid crystallized from ethanol in white needles, m.p. 260–260.5°.

Anal. Calcd. for $C_{12}H_7NO_2$: C, 73.1; H, 3.6; N, 7.1. Found: C, 72.8; H, 3.6; N, 7.2.

Methyl 6-Bromo-1-naphthoate.—Mercuration of 3-bromonaphthalic anhydride and subsequent decomposition of the mercurated products with hydrochloric acid as described by Whitmore and Fox[7] produced a mixture of 3- and 6-bromonaphthoic acids. Several recrystallizations produced the pure 3-bromo-acid.

The mother liquors were evaporated to dryness and esterified with methanol and hydrogen chloride. Six recrystallizations of the crude ester produced pure **methyl 6-bromo-1-naphthoate** (2.3 g., 3.8% on bromonaphthalic anhydride), m.p. 63–64°.

Anal. Calcd. for $C_{12}H_9O_2Br$: C, 54.1; H, 3.4. Found: C, 54.1; H, 3.4.

Methyl 5-Cyano-2-naphthoate.—Methyl 5-bromo-2-naphthoate[23] (60 g.) was converted to the cyano-ester by the method described for the 3-cyano-1-naphthoate. Crystallization of the crude product from dilute ethanol gave **methyl 5-cyano-2-naphthoate** as white needles, m.p. 114.5–115° (31 g., 65%).

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.9; H, 4.3; N, 6.6. Found: C, 74.3; H, 4.3; N, 6.7.

5-Cyano-2-naphthoic Acid Hydrazide.—Methyl 5-cyano-1-naphthoate (30 g.) and hydrazine hydrate (30 g.) were refluxed in absolute ethanol (150 ml.) for 15 hours. On cooling the **5-cyano-2-naphthoic acid hydrazide** crystallized in very pale yellow needles (27.5 g., 92%), m.p. 192–194°. A sample crystallized from ethanol had m.p. 194°.

Anal. Calcd. for $C_{12}H_9N_3O$: C, 68.2; H, 4.3; N, 19.9. Found: C, 67.8; H, 4.3; N, 19.7.

5-Cyano-2-naphthoic Acid Azide.—The corresponding hydrazide (25 g.) was dissolved in glacial acetic acid (500 ml.) and water (200 ml.). Crushed ice (100 g.) was added and the solution treated with a solution of sodium nitrite (9.0 g.) in water with vigorous stirring. The precipitated acid azide was filtered and washed with water. The azide was dried first between filter papers and finally in small batches in a vacuum desiccator. 5-Cyano-2-naphthoic acid azide had m.p. 133° with violent decomposition.

5-Cyano-2-naphthylamine (1-Cyano-6-naphthylamine).—To stirred concentrated sulfuric acid (200 ml.) was added in portions the azide of 5-cyano-2-naphthoic acid (20 g.), the temperature being kept at 40°. Crushed ice (500 g.) and ammonium hydroxide (d. 0.880) were added until the solution was alkaline to litmus. One recrystallization of the crude amine (10.2 g. 67.5%) from dilute ethanol gave pure **1-cyano-6-naphthylamine** as yellow needles, m.p. 142.5–143°.

Anal. Calcd. for $C_{11}H_8N_2$: C, 78.6; H, 4.7; N, 16.7. Found: C, 78.4; H, 4.8; N, 16.6.

1-Cyano-6-bromonaphthalene.—A solution of 1-cyano-6-naphthylamine (4 g.) in hot glacial acetic acid (45 ml.) was cooled to 10° and gradually stirred into a solution of sodium nitrite (2.5 g.) in sulfuric acid (15 ml.). This diazo solution was added to a well stirred solution of cuprous bromide (4 g.) in constant boiling hydrobromic acid (50 ml.); when evolution of nitrogen had ceased the solution was diluted with water (100 ml.) and the crude bromo compound filtered, washed and dried. Sublimation (110° (1 mm.)) afforded a white solid, m.p. 116–119° (2.4 g., 44%). Crystallization from petroleum ether (b.p. 80–100°) gave **1-cyano-6-bromonaphthalene** as white needles, m.p. 122–123°.

Anal. Calcd. for $C_{11}H_6BrN$: C, 56.9; H, 2.6; Br, 34.5; N, 6.0. Found: C, 57.0; H, 2.4; Br, 34.9; N, 6.3.

6-Bromo-1-naphthoic Acid.—A solution of 6-bromo-1-cyanonaphthalene (2 g.) in a mixture of glacial acetic acid (80 ml.), water (40 ml.) and concentrated sulfuric acid (40 ml.) was refluxed for 24 hours. The white precipitate was washed, extracted into sodium carbonate solution, and acidified, giving the crude acid (1.9 g., 88%). Recrystallization from dilute ethanol gave pure **6-bromo-1-naphthoic acid** in white needles, m.p. 185–186°.

Anal. Calcd. for $C_{11}H_7BrO_2$: C, 52.6; H, 2.8; Br, 31.8. Found: C, 52.8; H, 2.8; Br, 31.7.

Esterification of a sample with diazomethane gave the methyl ester, identical with that prepared above.

Methyl 6-Cyano-1-naphthoate.—Prepared from the bromo-ester by the method described for the 3-isomer, the ester crystallized from petroleum ether (b.p. 80–100°) in white needles, m.p. 131–131.5° (76% yield).

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.9; H, 4.3. Found: C, 74.3; H, 4.4.

6-Cyano-1-naphthoic Acid.—The methyl ester was hydrolyzed by the method described for the 3-isomer. **6-Cyano-1-naphthoic acid** crystallized from dilute methanol in white needles, m.p. 284–286° dec.

Anal. Calcd. for $C_{12}H_7NO_2$: C, 73.1; H, 3.6; N, 7.1. Found: C, 72.9; H, 3.9; N, 7.2.

7-Nitro-1-naphthoic Acid.—7-Amino-1-naphthoic acid[10] (1 g.) in dilute sodium hydroxide (25 ml., 0.2 *N*) containing sodium nitrite (0.3 g.) was added slowly to dilute sulfuric acid (10 ml., 2 *N*) keeping the temperature between 10–12°. Urea was added to destroy excess nitrous acid, the solution filtered and the filtrate added portionwise to a solution of sodium nitrite (20 g.), copper sulfate (4 g.), sodium bicarbonate (5 g.), cuprous oxide (1.5 g.) and water (50 ml.) at 80°. The resulting suspension was stirred for 1 hour and acidified with dilute hydrochloric acid. The crude **7-nitro-1-naphthoic acid**, after extraction with sodium carbonate and acidification, sublimed at 240° (0.1 mm.) as a yellow solid (0.4 g., 36%) which crystallized from nitromethane in pale yellow needles, m.p. 266.5–267.5° (lit.[32] 261–263.5°).

Anal. Calcd. for $C_{11}H_7NO_4$: C, 60.8; H, 3.2; N, 6.5. Found: C, 60.9; H, 3.2; N, 6.5.

7-Methyl-1-naphthoic Acid.—The Grignard reagent from 7-methyl-1-bromonaphthalene[28] was poured onto solid carbon dioxide. The corresponding acid was isolated in the usual way. It crystallized from dilute ethanol in white needles, m.p. 146–147° (lit.[33] 147–148°).[11]

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.4; H, 5.4. Found: C, 77.2; H, 5.3.

Methyl 7-Cyano-1-naphthoate.—Methyl 7-bromo-1-naphthoate was converted to the **cyano-ester** and purified by the

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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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