538. *Dissociation Constants of Some Methylnaphthoic and Acenaphthoic Acids.*

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pK values have been determined, in 20% (by weight) dioxan, for aromatic monocarboxylic acids derived from naphthalene, 1-methylnaphthalene, 1,8-dimethylnaphthalene, and acenaphthene. Both the pK values and the ultraviolet spectral data are in accord with the order of increasing steric effect: ethylene bridge < 1-methyl < 1,8-dimethyl.

Acenaphthene, 1-methylnaphthalene, and 1,8-dimethylnaphthalene form a series in which the steric and electronic effects of the alkyl substituents are expected to fall into different sequences. Information on these substituent effects should be given by the dissociation constants of the derived carboxylic acids and we report thermodynamic pK values for the three acenaphthoic acids, the three 1,8-dimethylnaphthoic acids, and 1-methyl-2-, 4-methyl-2-, 4-methyl-1-, and 5-methyl-1-naphthoic acid. Relevant ultraviolet spectral data are also reported.

Experimental

Microanalyses were carried out by the Microanalytical Laboratory (Dr. A. D. Campbell) of the University of Otago.

Methylnaphthoic Acids.—(*a*) 1-*Methyl*-2-*naphthoic acid.* To a stirred suspension of 2-dimethylaminomethyl-1-methylnaphthalene [1] (5·0 g.; b. p. 118—122°/1 mm.) in water (150 ml.) was added (3 hr.) finely powdered potassium permanganate (10·0 g.). The mixture was stirred for a further 2 hr. and the manganese dioxide formed was filtered off. Acidification of the filtrate afforded the required acid (2·1 g., 45%), m. p. 179·5—180°.

When alkaline permanganate [1] was used for the oxidation, lower yields of the acid were obtained, and also isolated, by means of ether, was 1-*methyl*-2-*naphthaldehyde*, b. p. 117—125°/1 mm., m. p. 45° (Found: C, 84·5; H, 5·6. $C_{12}H_{10}O$ requires C, 84·65; H, 5·9%). The aldehyde gave a 2,4-dinitrophenylhydrazone, m. p. 270° (from dioxan).

(*b*) 4-*Methyl*-2-*naphthoic acid.* Diethyl allylbenzylmalonate was obtained (47%) from diethyl malonate by successive condensations with benzyl bromide [2] and allyl bromide; condensations carried out in the reverse order gave the product in only 29% yield.[3] The allylbenzylmalonate was converted [3] into 2-benzylpent-4-enoic acid (83%), b. p. 127—129°/0·5 mm., n_D^{25} 1·5177. A mixture of the acid (20 g.), sulphuric acid (36 g.), and water (24 g.) was stirred for 7 days at 50—55°. It was then poured into 12% sodium carbonate solution (400 ml.), the alkaline solution was washed with ether (2 × 200 ml.), and the ether then extracted with 2N-sodium hydroxide (100 ml.). The combined alkaline liquors were acidified, and the resulting precipitate was recrystallised from acetic acid to give white needles of 1,2,3,4-tetrahydro-4-methyl-2-naphthoic acid (6·1 g., 30%), m. p. 115—118°; vacuum distillation of the product gave material of b. p. 172—175°/2 mm., m. p. 119—120°. [Darzens [4] reported that the action of aqueous (65%) sulphuric acid, for 8 days at 120—125°, led to quantitative isomerisation of the 2-benzylpentenoic acid but, in an attempt to repeat this, we obtained only a 21% yield of the tetrahydromethylnaphthoic acid.]

The tetrahydromethylnaphthoic acid (4·75 g.) was heated at 200° for 6 hr. with sulphur (1·62 g.), the mixture was poured into 10% sodium carbonate solution (200 ml.), and the alkaline solution then filtered. Acidification of the filtrate afforded a precipitate which gave 4-methyl-2-naphthoic acid (2·2 g., 48%) as needles m. p. 196—200° (from acetic acid) (raised to 202—203° after two further recrystallisations).

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[1] Hauser, Van Eenam, and Bayless, *J. Org. Chem.*, 1958, **23**, 354.

[2] Marvel, *Org. Synth.*, 1941, **21**, 99.

[3] Arnold, Campos, and Lindsay, *J. Amer. Chem. Soc.*, 1953, **75**, 1044.

[4] Darzens, *Compt. rend.*, 1930, **190**, 1305.

(*c*) 4-*Methyl*-1-*naphthoic acid.* This was obtained (70%) from 4-bromo-1-methylnaphthalene [6] *via* the lithium compound. It had m. p. 175—176·5° (from aqueous ethanol).

(*d*) 5-*Methyl*-1-*naphthoic acid.* Dewar and Grisdale [7] have recently obtained this acid by a four-stage preparation from methyl 5-bromo-1-naphthoate. Unaware of this work, we chose a two-step route from commercial 1,5-dimethylnaphthalene. *N*-Bromosuccinimide (28·5 g.), benzoyl peroxide (0·25 g.), and 1,5-dimethylnaphthalene (25 g.) were refluxed in carbon tetrachloride (100 ml.) for 3 hr. (There is an initial vigorous reaction on heating.) The mixture was then cooled, carbon tetrachloride (100 ml.) was added, and the precipitate filtered off. The filtrate was washed with 0·5% sodium hydroxide solution and with water, and dried ($MgSO_4$). After removal of solvent, vacuum-fractionation afforded 1-*bromomethyl*-5-*methylnaphthalene* (16·4 g., 43·5%), b. p. 186—194°/16 mm., m. p. 61·5° (from ethanol) (Found: C, 60·7; H, 4·3. $C_{12}H_{11}Br$ requires C, 61·2; H, 4·65%). The precipitate obtained from the carbon tetrachloride solution was washed with aqueous alkali and with water, dried, and recrystallised from benzene to give 1,5-dibromomethylnaphthalene (9·0 g.), m. p. 211° (lit.,[8] m. p. 212°).

To the 1-bromomethyl-5-methylnaphthalene (5 g.), in dioxan (40 ml.), was added aqueous hypobromite (5 ml. of bromine dissolved in 40 g. of 25% aqueous sodium hydroxide) and the mixture stirred for 5 hr. at 50° and allowed to cool. Water was added and the mixture was extracted with ether (2 × 100 ml.). The ethereal extract was washed with 10% sodium hydroxide solution (50 ml.); the total alkaline aqueous-liquors were heated to remove any ether and then acidified. 5-Methyl-1-naphthoic acid (1·0 g.) was deposited, having m. p. 192° (from aqueous acetic acid) (lit.,[7] 188—189°) (Found: C, 77·5; H, 5·1; O, 16·9. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4; O, 17·2%).

Dimethylnaphthoic Acids.[9]—The following were used: 1,8-, m. p. 122—123° (from aqueous ethanol), and 4,5-dimethyl-2-naphthoic acid, m. p. 222° (from acetic acid); 4,5-dimethyl-1-naphthoic acid, m. p. 194·5—196·5° (from aqueous dioxan).

Acenaphthoic Acids.—(*a*) 3-*Acenaphthoic acid.* A solution of 3-propionylacenaphthene [10] (20·0 g.) in dioxan (1 l.) and water (500 ml.) was heated at 60° for 45 min. with a solution of sodium hypobromite (made at 0—10° by stirring 87·5 g. of bromine with a solution of 87·5 g. of sodium hydroxide in 360 ml. of water). The mixture was then refluxed for 45 min., after which a similar amount of hypobromite solution was added and the mixture refluxed for 1 hr. The two layers were then separated, and sulphur dioxide was passed through the lower, aqueous layer to precipitate the required acid. A further quantity of product was obtained by addition of the upper layer to water (2 l.) followed by passage of sulphur dioxide through this mixture. The product (14·0 g., 75%), m. p. 252—256°, was recrystallised successively from ethanol, acetic acid, and aqueous dioxan to give colourless needles, m. p. 258—260°.

(*b*) 4-*Acenaphthoic acid.* Phosphorus tribromide (7·4 g.), in anhydrous ether (50 ml.), was added during 2 hr. to a stirred solution of 3-bromo-1,8-di(hydroxymethyl)naphthalene [9] (8·75 g.) in benzene (120 ml.) and anhydrous ether (25 ml.). The mixture was refluxed for 1 hr., and then poured on ice (250 g.). The organic layer was decanted, washed with saturated sodium hydrogen carbonate solution followed by water, and dried ($MgSO_4$). Removal of the solvent, followed by two recrystallisations of the residue from benzene–light petroleum (b. p. 100—120°) gave 3-*bromo*-1,8-*di*(*bromomethyl*)*naphthalene* (10·3 g., 80%) as colourless prisms, m. p. 130—131·5° (Found: C, 36·55; H, 2·35; Br, 60·8. $C_{12}H_9Br_3$ requires C, 36·7; H, 2·3; Br, 61·0%). A solution of this compound (15·5 g.) in anhydrous benzene (300 ml.) was placed in a 500-ml. 3-necked flask, fitted with a sealed stirrer, dropping funnel, and reflux condenser. After the apparatus had been flushed with nitrogen, ethereal phenyl-lithium [11] (10% excess, 0·5N) was added dropwise to the stirred mixture. Stirring was continued for 30 min. at room temperature and for a further 1 hr. while the mixture was being refluxed. The mixture was poured into water (500 ml.) and acidified with dilute hydrochloric acid. The aqueous layer was then washed with benzene and the combined organic liquids were washed with water and dried

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[5] Darzens, *Compt. rend.*, 1926, **183**, 748.
[6] Topsom and Vaughan, *J.*, 1957, 2842.
[7] Dewar and Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3541.
[8] Ried and Bodem, *Chem. Ber.*, 1958, **91**, 1981.
[9] Mitchell, Topsom, and Vaughan, *J.*, 1961, 2526.
[10] Wade and Peters, *J.*, 1958, 3504.
[11] Jones and Gilman, *Org. Reactions*, 1951, **7**, 353.

($MgSO_4$). Organic solvent was then removed and vacuum-fractionation of the residue gave 4-bromoacenaphthene (6·2 g., 67·5%), b. p. 140—142°/0·5 mm., m. p. 65—65·5° (from ethanol–methanol) [picrate, m. p. 76·5—78° (lit.,[12] m. p. 77—79°)]. The bromo-compound was converted (65%) into *4-acenaphthoic acid* by treatment with n-butyl-lithium (50% excess; 1·25N) and subsequent carbonation. The acid had m. p. 207—210° (decomp.) (from acetic acid and from aqueous dioxan) (Found: C, 78·75; H, 5·3; O, 16·3. $C_{13}H_{10}O_2$ requires C, 78·75; H, 5·1; O, 16·15%).

(*c*) *5-Acenaphthoic acid.* 5-Bromoacenaphthene, m. p. 54° was prepared (57%) by the bromination[6] of acenaphthene. This was converted, *via* the lithium compound, into the required acid (52%). Successive recrystallisations from acetic acid, ethanol, and aqueous methanol gave needles, m. p. 221—223°.

Dissociation Constants.—These were determined by the spectrophotometric method, using a Hilger "Uvispek" instrument. The quartz cells (4 cm. path) were kept at 25·0° ± 0·2°. The acids were not sufficiently soluble in water for our purpose, and measurements were made in 20% (by weight) dioxan. In this solvent the thermodynamic dissociation constants of the buffer acids, acetic acid (pK = 5·292) and formic acid (pK = 4·180), have been determined by Harned and his co-workers.[13]

The dissociation constants of the acids (HB) were evaluated by using the expression[14]

$$\mathrm{p}K_{\mathrm{HB}} = \mathrm{p}K_{\mathrm{HX}} + \log m_{\mathrm{X}}/m_{\mathrm{HX}} - \log m_{\mathrm{B}}/m_{\mathrm{HB}} - \log f_{\mathrm{B}}f_{\mathrm{HX}}/f_{\mathrm{HB}}f_{\mathrm{X}}$$

Since HX (the buffer acid) and HB represent acids of the same charge type, the activity coefficient term is proportional to I, the ionic strength, the proportionality constant being in fact zero, within the accuracy of the measurements, for all acids studied. Buffer ratios were 2 : 1, 1 : 1, or 1 : 2. For each acid, measurements were made at four ionic strengths. Detailed results for 1-methyl-2-naphthoic acid are given in Table 1.

TABLE 1.

pK value of 1-methyl-2-naphthoic acid in 20% (by weight) dioxan at 25°.

λ = 3300 Å, D_{HB} = 0·829, D_{B} = 0·084, C = 1·81 × 10^{-4}m.
Buffer, $H{\cdot}CO_2Na$: $H{\cdot}CO_2H$ = 2 : 1.

I	D	log $m_{\mathrm{B}}/m_{\mathrm{HB}}$	log $m_{\mathrm{X}}/m_{\mathrm{HX}}$	pK
0·01	0·430	0·0062	0·293	4·411
0·02	0·432	0·0057	0·297	4·420
0·03	0·430	0·0062	0·298	4·416
0·04	0·433	0·0055	0·299	4·424

Mean pK = 4·418.

TABLE 2.

pK values and spectral data (3300 Å band) of substituted naphthoic acids in 20% (by weight) dioxan at 25°.

Acid	pK	$\lambda_{\max.}$ (Å)	$\varepsilon_{\max.}$ (cm.$^{-1}$ l. mole^{-1})
1-Naphthoic	4·53	—	—
2-Naphthoic	4·89	3345	1600
4-Methyl-1-naphthoic	4·81	—	—
5-Methyl-1-naphthoic	4·57	—	—
1-Methyl-2-naphthoic	4·42	3265	1160
4-Methyl-2-naphthoic	4·98	3385	2010
4,5-Dimethyl-1-naphthoic	4·61	—	—
1,8-Dimethyl-2-naphthoic	4·25	3250	1430
4,5-Dimethyl-2-naphthoic	5·00	3465	2655
3-Acenaphthoic	5·49	3460	4000
4-Acenaphthoic	5·08	3445	2800
5-Acenaphthoic	5·30	—	—

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[12] Vorozhtsov and Tochilkin, *Nauch. Doklady Vysshei Shkoly, Khim. Khim. Tekhnol.*, 1959, **2**, 325 (*Chem. Abs.*, 1960, **54**, 445).

[13] Harned and Kazanjian, *J. Amer. Chem. Soc.*, 1936, **58**, 1912; Harned, *J. Phys. Chem.*, 1939, **43**, 275; Harned and Done, *J. Amer. Chem. Soc.*, 1941, **63**, 2579.

[14] Fickling, Fischer, Mann, Packer, and Vaughan, *J. Amer. Chem. Soc.*, 1959, **81**, 4226.

Repetition of the above determination on an independent solution of acid, a different buffer ratio (1 : 1), and a buffer solution prepared from a different batch of formic acid, gave a mean pK of 4·421. In general, agreement between separate determinations was within $\pm 0{\cdot}005$ pK unit. Mean pK values are estimated to be accurate to within $\pm 0{\cdot}03$ pK unit.

Reagents.—Dioxan was refluxed over sodium for 48 hr. and fractionally distilled. A centre fraction, b. p. 101·2°/758 mm., f. p. 11·9°, was diluted to 20% (by weight) for use as solvent.

"AnalaR" formic acid (90%) was fractionally distilled, and the middle fraction was standardised. "AnalaR" acetic acid was also fractionated, and had b. p. 118·2°/761 mm., f. p. 16·6° In the preparation of solutions, carbon dioxide-free water was used.

Results.—These are summarised in Table 2.

DISCUSSION

Acid Dissociation Constants.—Solvent effect. 1-Naphthoic acid is a stronger acid than the 2-isomer, this difference being a consequence of steric inhibition of resonance in the 1-acid. It has been observed [15] that the relative enhancement of acid strengths of *ortho*-substituted benzoic acids, and of hindered aliphatic acids, falls as the polarity of the solvent is lowered. A similar trend is apparent for the two naphthoic acids, ΔpK [= pK(1-naphthoic) — pK(2-naphthoic)] being —0·46 in water,[16] —0·36 in 20% dioxan (this paper), —0·06 in 50% butylcellosolve,[17] and —0·05 in 78% ethanol.[18] Factors which may contribute to this effect are: (1) a decrease in the importance of resonance-stabilisation of the undissociated 2-naphthoic acid (the consequent dipolar charges are not so readily dispersed by solvation); (ii) an increase in the sensitivity of the reaction to the electronic effects of substituents [σ(2,3-benzo) = —0·03; σ(3,4-benzo) = +0·04].[19,20]

Methyl-substituted naphthoic acids. Introduction of a 1-methyl substituent into 2-naphthoic acids lowers the pK value by 0·47 unit. For *o*-toluic acid [16] (compared with benzoic acid) ΔpK = —0·30 (in water). In both cases the methyl substituent sterically inhibits resonance-interaction of the carboxyl group with the aromatic ring, but the effect is greater in the naphthalene system because of buttressing by the adjacent *peri*-hydrogen. The effect of a 4-methyl group on the pK value of 2-naphthoic acid (ΔpK = 0·09) is similar to that of a *m*-methyl substituent on the pK value of benzoic acid (ΔpK = 0·07).[16] In the 1-naphthoic acid series, the 4-methyl group has a slightly greater effect (ΔpK = 0·28) than in the benzoic acids (ΔpK = 0·17); this result is consistent with the greater conjugative interactions between 4-($\pm M$) and 1-($\mp M$) substituents in the naphthalene series.[21,22] Substituents in the other ring of naphthalene exert only a small polar effect on functional groups in the first ring; [21,22] thus for 5-methyl-1-naphthoic acid, ΔpK is smaller (0·04). Dewar and Grisdale [23] have recently reported pK values for 4- and 5-methyl-1-naphthoic acids, in 50% (v/v) aqueous ethanol, which yield similar ΔpK values (0·21 for 4-methyl-1-naphthoic acid, and —0·02 for 5-methyl-1-naphthoic acid).

Dimethyl-substituted naphthoic acids. 1,8-Dimethyl-2-naphthoic acid (ΔpK = —0·64) is stronger than 1-methyl-2-naphthoic acid (ΔpK = —0·47); the 8-methyl substituent has a larger buttressing effect than the *peri*-hydrogen replaced by it. For 4,5-dimethyl-2-naphthoic acid (ΔpK = 0·11) the pK value is consistent with the value which would be predicted by a combination of the effect of the 4- and an expected smaller effect of a 5-substituent. However, for 4,5-dimethyl-1-naphthoic acid, ΔpK is only 0·08 instead of the 0·32 unit to be expected if an additivity relationship held. Stone and Pearson [24] have

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[15] Dippy, Hughes, and Rozanski, *J.*, 1959, 1441.

[16] Dippy, Hughes, and Laxton, *J.*, 1954, 1470.

[17] Berliner and Winicov, *J. Amer. Chem. Soc.*, 1959, **81**, 1630.

[18] Oae and Price, *J. Amer. Chem. Soc.*, 1957, **79**, 2547.

[19] Packer, Vaughan, and Wong, *J. Org. Chem.*, 1958, **23**, 1373.

[20] Fischer, Packer, Vaughan, Wilson, and Wong, *J. Org. Chem.*, 1959, **24**, 155.

[21] Creamer, Fischer, Mann, Packer, Richards, and Vaughan, *J. Org. Chem.*, 1961, **26**, 3148.

[22] Schreiber and Byers, *J. Amer. Chem. Soc.*, 1962, **84**, 859.

[23] Dewar and Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3546.

[24] Stone and Pearson, *J. Org. Chem.*, 1961, **26**, 257.

drawn attention to the possible breakdown in the additivity relationship for the polar effects of alkyl groups under severe steric compression.

Acenaphthoic acids. It is noteworthy that 3-acenaphthoic acid ($\Delta \mathrm{p}K = 0{\cdot}60$) is weaker than 2-naphthoic acid; among *ortho*-substituted benzoic acids only phthalic acid, in its second dissociation (a rather special case), is significantly weaker than benzoic acid. It appears that the ethylene bridge has both a low steric requirement and substantial electron-donating ability. *X*-Ray diffraction studies of acenaphthene [25] indicate that the binding of the methylene carbon atoms brings them nearer to each other by 0·4 Å; the spatial requirement of a methylene group in acenaphthene is less than that of a methyl group in 1-methylnaphthalene. The methylene group may in fact exert an acid-weakening steric effect, for as the size of an *ortho*-substituent is reduced it may at some stage become too small to inhibit conjugation in the acid but still be large enough to interfere with solvation in the anion. As to the electron-donor role of the ethylene bridge it appears that the C–H bonds are ideally placed for maximum overlap with the π-shell of the aromatic nucleus. Hyperconjugative electron donation should therefore be at a maximum. For 4-acenaphthoic acid, $\Delta \mathrm{p}K = 0{\cdot}19$, compared with 0·09 for 4-methyl-2-naphthoic acid, and 0·11 for 4,5-dimethyl-2-naphthoic acid. For 5-acenaphthoic acid (still with 1-naphthoic acid as reference acid), $\Delta \mathrm{p}K$ is again comparatively large (0·77).

Ultraviolet Spectra.—In the spectra of methylbenzoic acids [26] there are bands at 2050, 2300, and 2800 Å. Of these, the band at 2300 Å, the β band of Moser and Kohlenberg,[26] is most affected by *ortho*-substitution. Both the extinction coefficient and the wavelength of absorption are lowest for the *ortho*-substituted isomer.

Of the three spectral bands of 2-naphthoic acid, at *ca.* 2300, 2800, and 3300 Å, the last is most sensitive to "*ortho*"-substitution. Values of $\Delta\lambda_{\text{max.}}$ and $\Delta\varepsilon$ (reference acid is 2-naphthoic acid) and of $\Delta'\lambda_{\text{max.}}$ and $\Delta'\varepsilon$ (reference acid is the listed isomeric acid) are shown in Table 3. In the Δ' values, the normal small bathochromic and hyperchromic effects of alkyl substitution should be largely eliminated and these values should reflect the effect of steric inhibition of conjugation by the "*ortho*"-substituent.

TABLE 3.

Relative values of $\lambda_{\text{max.}}$ and $\varepsilon_{\text{max.}}$ for substituted 2-naphthoic acids.

Substituted acid	$\Delta\lambda_{\text{max.}}$	$\Delta\varepsilon_{\text{max.}}$	$\Delta'\lambda_{\text{max.}}$	$\Delta'\varepsilon_{\text{max.}}$
1-Methyl-2-naphthoic	−80	−440	−120	−850
4-Methyl-2-naphthoic	+40	+410	+120	+850
1,8-Dimethyl-2-naphthoic	−95	−170	−215	−1225
4,5-Dimethyl-2-naphthoic	+120	+1055	+215	+1225
3-Acenaphthoic	+115	+2400	+15	+1200
4-Acenaphthoic	+100	+1200	−15	−1200

The data in Table 3 show that, as measured both by the increasing hypsochromic and by the hypochromic effect of the "*ortho*"-substituted acid relative to its isomer, the order of increasing steric interference of such "*ortho*"-groups is ethylene bridge < 1-methyl < 1,8-dimethyl. This is the same order as that inferred from pK values. Further, just as 3-acenaphthoic acid is the only "*ortho*"-substituted 2-naphthoic acid which is weaker than 2-naphthoic acid, so also is 3-acenaphthoic acid the only one of the three to exhibit a bathochromic shift and a hyperchromic effect. All these results are a consequence of the small steric effect and the enhanced electron-donating ability of the acenaphthene bridge.

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[25] Erlich, *Acta Cryst.*, 1957, **10**, 699.
[26] Moser and Kohlenberg, *J.*, 1951, 804.