1114. *Dissociation Constants of Some Naphthylamines and Acenaphthenamines and their Dimethyl Derivatives*

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The pK values in water at 25° for 1- and 2-naphthylamine, their 4-methyl and 4,5-dimethyl derivatives, and 4- and 5-acenaphthenamine have been determined. The pK values, in 20% (by weight) dioxan, for the *NN*-dimethyl derivatives of these amines have also been determined.

We have recently reported dissociation constants of aromatic monocarboxylic acids derived from acenaphthene, 1-methylnaphthalene and 1,8-dimethylnaphthalene.[1] We have now measured the dissociation constants of the 3- and 4-amino- and dimethylamino-derivatives of the naphthalenes and the corresponding 4- and 5-derivatives of acenaphthene.

Experimental

Microanalyses were carried out by the Microanalytical Laboratory (Dr. A. D. Campbell) of the University of Otago. The purity of the arylamines and aryldimethylamines prepared was checked by vapour-phase chromatography (v.p.c.).

Methylnaphthylamines.—(*a*) 4-*Methyl*-1-*naphthylamine*. 4-Nitro-1-methylnaphthalene [2] was reduced with aluminium amalgam [3] to give the amine, m. p. 51·5—52° (from light petroleum, b. p. 50—70°) (lit.,[4] 51—52°).

(*b*) 4-*Methyl*-2-*naphthylamine*. This arylamine has been prepared [5] by a lengthy procedure from 1-methylnaphthalene. We used a two-step process from the same starting material. 1-Methylnaphthalene was converted [6] into 1-bromo-4-methylnaphthalene which was treated with potassium amide in liquid ammonia to give a mixture of 4-methyl-1- and 4-methyl-2-naphthylamine. The predominance of the latter was in accord with corresponding work with 1-bromonaphthalene [5,7] and 5-bromoacenaphthene.[8]

Potassium (8 g.) in liquid ammonia (300 ml.) was stirred wth trace quantities of ferric nitrate hydrate and ferric oxide for 8 hr. 1-Bromo-4-methylnaphthalene (30 g.) was stirred, in another flask, with anhydrous ether (200 ml.) and liquid ammonia (150 ml.) until solution was complete. The potassium amide solution was then forced, as rapidly as possible, into the second flask by a stream of dry nitrogen. (The rate of addition was limited by the boiling of the reaction mixture.) After 10 min., ammonium nitrate (50 g.) was added and the ammonia was allowed to evaporate. Water (400 ml.) was added and the mixture was extracted with ether (1 × 200 ml., 3 × 100 ml.), and the ether then extracted with hydrochloric acid (5N, 1 × 100 ml., 4 × 50 ml.). The combined acidic liquors were made alkaline and the liberated amines were extracted into ether (1 × 200 ml., 4 × 50 ml.), and the ether then washed with water and dried ($MgSO_4$). After removal of solvent, vacuum distillation gave a solid (7·6 g.) of low melting-point, b. p. 123—130°/1 mm. This mixture of amines was acetylated by heating to 110° for

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[2] H. W. Thompson, *J.*, 1932, 2310.
[3] G. T. Morgan and H. A. Harrison, *J. Soc. Chem. Ind.*, 1930, **49**, 413T.
[4] R. Lesser, A. Glaser, and G. Aczel, *Annalen*, 1913, **402**, 1.
[5] J. Sauer, R. Huisgen, and A. Hauser, *Chem. Ber.*, 1958, **91**, 1461.
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[7] R. S. Urner and F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1945, **67**, 2108.
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10 min. with acetic anhydride (7·5 ml.) and glacial acetic acid (50 ml.). The solution was cooled and added to aqueous sodium hydroxide (20%; 250 ml.). The acetylamines were filtered off, washed with water, and dried. They were dissolved in a mixture of benzene (100 ml.) and acetone (15 ml.) and chromatographed on activated alumina (600 g.), ether being used as an eluent. The first fraction was *N*-acetyl-4-methyl-2-naphthylamine (5·3 g., 19·5%), m. p. 172—173° (from ethanol) (lit.,[9] 172—173°). The second fraction was *N*-acetyl-4-methyl-1-naphthylamine (2·7 g., 10%), m. p. 166—167° (from ethanol) not depressed by the addition of an authentic sample.

4,5-*Dimethylnaphthylamines*.—(*a*) 4,5-*Dimethyl*-1-*naphthylamine*. 1,8-Dimethylnaphthalene [10] was treated with nitric acid in acetic acid to give 1-nitro-4,5-dimethylnaphthalene, m. p. 64—65° (from ethanol), which was converted into the required amine, m. p. 85·5—86° (from light petroleum, b. p. 50—70°), by reduction with aluminium amalgam. Both compounds have recently been reported.[11] The amine was acetylated to give N-*acetyl*-4,5-*dimethyl*-1-*naphthylamine*, m. p. 185—185·5° (from ethanol) (Found: C, 78·6; H, 6·9; N, 6·5. $C_{14}H_{15}NO$ requires C, 78·85; H, 7·1; N, 6·55%).

(*b*) 4,5-*Dimethyl*-2-*naphthylamine*. 2-Bromo-4,5-dimethylnaphthalene [10] (10 g.; m. p. 90—91°) in anhydrous ether (150 ml.) was added over 5 min. to a solution of n-butyl-lithium [12] in ether (65 ml., 48% excess) contained in a 250-ml. 3-necked flask fitted with a sealed stirrer, dropping funnel, and a reflux condenser. (The reaction was performed in an atmosphere of nitrogen.) After 5 min., anhydrous cadmium chloride (6·2 g.) was added and the reaction mixture was refluxed (water-bath) with stirring for 6 hr. The ether was then distilled off while anhydrous benzene (150 ml.) was added. Redistilled acetyl chloride (6·0 g.) in anhydrous benzene (25 ml.) was quickly added to the cool, stirred mixture, and the whole then heated (water-bath) to 80° over a period of 1 hr. and then refluxed for 30 min. The mixture was cooled and added to aqueous sulphuric acid (3%; 200 ml.). Benzene (250 ml.) was added, and the organic layer was washed with water and dried ($MgSO_4$). After removal of the solvent, vacuum distillation gave an oil (5·8 g.), b. p. 144—164°/1 mm., which was chromatographed on activated alumina (250 g.). The first fraction, eluted with light petroleum (b. p. 55—65°), was 1,8-dimethylnaphthalene (0·92 g., 14%), identical with an authentic sample. A mixture of equal parts of light petroleum (b. p. 55—56°) and benzene eluted 2-*acetyl*-4,5-*dimethylnaphthalene* (3·7 g., 44%), m. p. 43—44° (from ethanol). A second recrystallisation gave material, m. p. 45—46° (Found: C, 85·05; H, 7·15; N, 8·25. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1; N, 8·1%). The 2,4-*dinitrophenylhydrazone* had m. p. 280—281·5° (from dioxan).

2-Acetyl-4,5-dimethylnaphthalene (1·13 g.) was heated to 60° with dry trichloroacetic acid (20 g.), and sodium azide (1 g.) was added. The mixture was kept at 60—65° for 1 hr. and then poured into water (60 ml.). This was cooled in ice and ammonia (0·880, 20 ml.) was added. The precipitate was N-*acetyl*-4,5-*dimethyl*-2-*naphthylamine* (1·17 g., 96%), m. p. 187—190° raised to 192—193° by recrystallisation from benzene (Found: C, 79·35; H, 7·0; N, 6·9. $C_{14}H_{15}NO$ requires C, 78·85; H, 7·1; N, 6·6%). This compound (10·0 g.) was refluxed for 3 hr. with concentrated hydrochloric acid (12 ml.) and ethanol (100 ml.). The solution was cooled, ether (600 ml.) added, and the resultant precipitate was filtered off, washed with ether, and dried to give 9·2 g. (94%) of 4,5-*dimethyl*-2-*naphthylamine hydrochloride* (Found: C, 70·2; H, 7·1; N, 6·25. $C_{12}H_{14}NCl$ requires C, 69·4; H, 6·8; N, 6·75%). The hydrochloride (7·2 g.) was neutralised by shaking with aqueous sodium hydroxide and ether. Distillation gave 5·4 g. (91%) of 4,5-*dimethyl*-2-*naphthylamine*, b. p. 157—161°/1 mm., m. p. 95—95·5 (from aqueous methanol) (Found: C, 83·8; H, 7·7. $C_{12}H_{13}N$ requires C, 84·15; H, 7·65%).

Acenaphthenamines.—(*a*) 5-*Acenaphthenamine*. A pure sample of this compound was not obtained by reduction of 5-nitroacenaphthene because the latter could not be freed from an impurity found (v.p.c.) in two samples prepared by different methods.[13,14] Reduction gave a mixture of amines (the original impurity probably being 3-nitroacenaphthene) which again

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[11] L. I. Denisova, N. A. Morosova, V. A. Plakhov, and A. I. Tochilkin, *Zhur. obshchei Khim.*, 1964, **34**, 519.
[12] R. G. Jones and H. G. Gilman, "Organic Reactions," John Wiley and Sons, Inc., New York, 1951, vol. 6, p. 352.
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could not be completely separated. 5-Bromoacenaphthene [6] was equally difficult to purify but 5-acenaphthoic acid [6] proved to be a suitable starting material. Phosphorus pentoxide (21 g.) was heated to 200° with orthophosphoric acid (90%, 20 g.) until the mixture was homogeneous (*ca.* 3 hr.). 5-Acenaphthoic acid (3 g.) was stirred into the mixture and sodium azide (4 g.) added. The mixture was allowed to stand overnight and was then heated to 120° (oil-bath) until effervescence ceased (*ca.* 45 min.). It was then cooled and poured into aqueous potassium hydroxide (10%; 500 ml.) and the product was extracted with ether (3 × 200 ml.). The ether was washed with water, dried ($MgSO_4$), and the solvent removed. Vacuum distillation of the residue gave 5-acenaphthenamine (0·55 g., 22%), b. p. 158—166/1 mm., m. p. 107·5—108° (from aqueous methanol) (lit.,[14] 108°). [The yield was lower than that reported [15] for similar reactions with benzoic acids (50—90%) but this probably results from the low solubility of the acenaphthoic acid in the polyphosphoric acid; the yield with 1-naphthoic acid was 40%.]

(*b*) 4-*Acenaphthenamine.* 4-Bromoacenaphthene [1] was converted into 4-*acetylacenaphthene* as described above for the preparation of 4-acetyl-4,5-dimethylnaphthalene. The product (20%) had m. p. 81—83° (from ethanol) raised to 86·5—87·5° (from light petroleum, b. p. 55—65°) (Found: C, 85·7; H, 5·8; O, 8·3. $C_{14}H_{12}O$ requires C, 85·7; H, 6·15; O, 8·15%). It gave a 2,4-*dinitrophenylhydrazone*, m. p. 300° (decomp.) (Found: C, 63·65; H, 4·7; N, 15·5. $C_{20}H_{16}N_4O_4$ requires C, 63·8; H, 4·3; N, 14·9%). This acetyl compound was converted (71%) into *N*-acetyl-4-acenaphthenamine as described for the corresponding 4,5-dimethylnaphthalene derivative. It had m. p. 175—176° (from aqueous ethanol) (lit.,[14] 175—176°). Hydrolysis gave 4-acenaphthenamine (64%).

NN-*Dimethylarylamines.*—The six amines described above were converted into their NN-dimethyl derivatives by treatment with equimolar amounts of trimethylphosphate.[16] Thus were obtained: 4-*methyl*-1-*dimethylaminonaphthalene* (64%), b. p. 137—139° (Found: C, 84·29; H, 8·24; N, 7·56. $C_{13}H_{15}N$ requires C, 84·3; H, 8·15; N, 7·55%); 4-*methyl*-2-*dimethylaminonaphthalene* (11% after distillation and chromatography on alumina), b. p. 136—138/1 mm. (Found: C, 84·3; H, 8·4; N, 7·6. $C_{13}H_{15}N$ requires C, 84·3; H, 8·15; N, 7·55%); 4,5-*dimethyl*-1-*dimethylaminonaphthalene* (60%), b. p. 142—144°/1 mm. (Found: C, 83·95; H, 8·6; N, 6·2. $C_{14}H_{17}N$ requires C, 84·35; H, 8·6; N, 7·05%); 4,5-*dimethyl*-2-*dimethylaminonaphthalene* (17·5% after distillation and several recrystallisations from aqueous methanol), b. p. 148—152°/1 mm., m. p. 56—57° (Found: C, 84·0; H, 8·9; N, 6·95. $C_{14}H_{17}N$ requires C, 84·35; H, 8·6; N, 7·05%); 5-dimethylaminoacenaphthene, b. p. 151—152°/1 mm., m. p. 45·5—46·5° (lit.,[17] m. p. 45—46°)(Found: C, 85·15; H, 7·9; N, 7·35. Calc. for $C_{14}H_{15}N$: C, 85·25; H, 7·65; N, 7·1%); 4-*dimethylaminoacenaphthene* (18·5% after distillation, chromatography on alumina and recrystallisation from light petroleum, b. p. 55—65°), b. p. 154—158°/1 mm., m. p. 53—54° (Found: C, 85·35; H, 7·6; N, 7·5. $C_{14}H_{15}N$ requires C, 85·25; H, 7·65; N, 7·1%).

Reagents.—Dioxan (10 l.) was refluxed for 12 hr. with 1M-hydrochloric acid. Tin (50 g.) was added and the mixture refluxed for a further 12 hr. The solution was saturated with potassium hydroxide and the aqueous layer separated. After being dried over potassium hydroxide and then over sodium the dioxan was refluxed over sodium for 1 week and then fractionally distilled. A centre fraction (5 l.), b. p. 101·0°/755 mm. (101·3°/760 mm.),[18] was diluted to 20% (by weight) for use as solvent. AnalaR acetic acid was fractionally distilled, b. p. 117·4—117·5°/756 mm. (117·7°/760 mm.).[18] AnalaR formic acid (90%) was also fractionated, b. p. 100·4—100·7°/760 mm. (100·7°/760 mm.).[18] Carbon dioxide-free water was used for preparation of solutions. Buffer solutions in both 20% dioxan and in water were made by weight from standardised solutions of sodium hydroxide and buffer acid in the appropriate solvent. All solvents and solutions were protected from carbon dioxide absorption by soda lime guard tubes.

Stock solutions of amines from which the amine solutions for spectrophotometry were obtained by dilution were made from the hydrochlorides rather than from the free bases which were difficultly soluble. Each primary amine was converted into its hydrochloride by passing

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[18] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, " Organic Solvents," Interscience, New York, 1955.

dry hydrogen chloride through an ethereal solution. The precipitated salt was filtered off, washed with ether, and dried. The hydrochloride of 2-dimethylaminonaphthalene appeared to be unstable so the tertiary amine hydrochlorides were not isolated. Methanol (1 ml.) was added to dissolve the tertiary amine followed by the stoicheiometric amount of hydrochloric acid in 20% dioxan. The solutions used for spectrophotometric measurements contained, after dilution, less than 0·1% methanol, insufficient to affect the measured pK values.

Dissociation Constants.—The spectrophotometric method was used as described previously.[1] Detailed results for a single pK determination for 1-naphthylammonium ion are given in Table 1 ($\phi(I^{\frac{1}{2}}) = 1{\cdot}02\ I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$).

TABLE 1

pK value of 1-naphthylammonium ion in water at 25°

$\lambda = 325$ mμ, $D_{HB} = 0{\cdot}003$, $D_B = 0{\cdot}821$, $C = 1{\cdot}92 \times 10^{-4}m$

Buffer $CH_3CO_2Na : CH_3CO_2H = 1 : 3{\cdot}06$.

I	D	$-\log m_X/m_{HX}$	$\log m_B/m_{HB}$	$\phi(I^{\frac{1}{2}})$	pK'
0·008	0·530	0·490	0·258	0·085	3·923
0·016	0·519	0·488	0·233	0·115	3·920
0·024	0·511	0·487	0·215	0·137	3·917
0·032	0·505	0·487	0·201	0·155	3·913

Extrapolated pK = 3·926.

Determinations of pK were usually repeated several times; the wavelength at which optical densities were measured, the buffer ratio, and the buffer acid (formic or acetic) [19] itself were all varied. Duplicate pK values measured at the same wavelength did not differ by more than ±0·02. Values did vary slightly with wavelength; variations of up to 0·02 were observed for wavelengths differing by 15 mμ. The total range of pK values for any one compound, however, never exceeded 0·033.

Mean pK values are estimated to be accurate to ±0·02 and are shown in Table 2.

TABLE 2

Dissociation of substituted naphthylammonium ions in water at 25° and of substituted naphthyldimethylammonium ions in 20% (by weight) dioxan at 25°

Parent amine	pK
1-Naphthylamine	3·94
2-Naphthylamine	4·20
4-Methyl-1-naphthylamine	4·37
4-Methyl-2-naphthylamine	4·31
4,5-Dimethyl-1-naphthylamine	4·42
4,5-Dimethyl-2-naphthylamine	4·27
5-Acenaphthenamine	4·58
4-Acenaphthenamine	4·50
1-Dimethylaminonaphthalene	4·43
2-Dimethylaminonaphthalene	4·36
4-Methyl-1-dimethylaminonaphthalene	4·73
4-Methyl-2-dimethylaminonaphthalene	4·57
4,5-Dimethyl-1-dimethylaminonaphthalene	4·74
4,5-Dimethyl-2-dimethylaminonaphthalene	4·53
5-Dimethaminoacenaphthene	5·07
4-Dimethylaminoacenaphthene	4·92

DISCUSSION

There is good agreement between the present pK values for 1- and 2-naphthylamine and earlier values of 3·92 and 4·11—4·27, respectively.[20] 1-Naphthylamine is a weaker base than its 2-isomer by 0·26 pK unit. Relative to phenyl the 1-naphthyl group has a positive inductive effect ($\sigma^* = -0{\cdot}03$) and the 2-naphthyl group a negative one ($\sigma =$

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[20] N. F. Hall and M. R. Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469; A. Bryson, *ibid.*, 1960, **82**, 4862; R. C. Farmer and F. J. Warth, *J.*, 1904, 1713.

+0·04).† From the polar (inductive) effect it would be expected that 1-naphthylamine would be a stronger base than 2-naphthylamine by *ca.* 0·2 pK unit since, for anilinium ion dissociation,[23] $\rho = 2{\cdot}8$. Two factors operating against the inductive effect are (i) greater resonance stabilisation of 1- than 2-naphthylamine and (ii) steric inhibition of solvation in 1-naphthylammonium ion. Factor (ii) is probably the more important. The steric effect of a *peri*-H exceeds that of an *ortho*-CH_3.[24] *o*-Toluidine is *ca.* 0·7 pK unit weaker as a base than *p*-toluidine,[25] a difference which can largely be attributed to steric inhibition of solvation in the cation conjugate acid.

1-Dimethylaminonaphthalene is a slightly stronger base than its 2-isomer. Steric inhibitionof resonance in *ortho*-substituted *NN*-dimethylanilinesis well established and there is direct evidence for such steric inhibition in 1-dimethylaminonaphthalene.[26] This should make the 1-dimethylaminonaphthalene a stronger base than its 2-isomer. Although solvation is much less extensive in tertiary than in primary ammonium ions, severely hindered tertiary ammonium ions do exhibit steric inhibition of solvation.[27] It is proposed that the base-strengthening effect of steric inhibition of resonance in 1-dimethylaminonaphthalene is outweighed by inhibition of solvation in the cation, the net result being that 1-dimethylaminonaphthalene is only a slightly stronger base than the 2-isomer.

Methyl-substituted Amines.—4-Methyl-2-naphthylamine and 4-methyl-2-dimethylaminonaphthalene are stronger bases than the parent amines by 0·11 and 0·21 pK unit, respectively. The effect of the 4-methyl substituent is comparable with that of a *meta*-methyl substituent in the corresponding benzene derivatives where it is base-strengthening by 0·15 (anilines) [25] and 0·27 (dimethylanilines) [28] pK unit. The greater sensitivity of the dimethylamino-compounds to the effect of the methyl substituent is qualitatively consistent with the greater rho-value for the dimethylaniline reaction. However, whereas a 4-methyl group introduced into 1-naphthylamine raises the pK by 0·43 unit a smaller effect, 0·30 unit, is evident in 4-methyl-1-dimethylaminonaplthalene. In the benzene series the pK elevations of 0·50 (4-methylaniline) [25] and 0·56 (dimethyl-*p*-toluidine) [28] followed the expected order. The reduced effect of the 4-methyl group on the pK of the 1-dimethylaminonaphthalene may reflect some general property of hindered systems. Whereas the introduction of a 4-methyl group into dimethylaniline raises the pK by 0·56 the similar substitution of a 4-methyl group into dimethyl-*o*-toluidine results in a much smaller pK elevation (0·21).[29]

Dimethyl-substituted Amines.—4,5-Dimethyl-1-naphthylamine is a stronger base than 4-methyl-1-naphthylamine by 0·05 pK unit. 4,5-Dimethyl-1-dimethylaminonaphthalene is insignificantly stronger (0·01) than 4-methyl-1-dimethylaminonaphthalene. However, introduction of a 5-methyl substituent into 4-methyl-2-naphthylamine and into 4-methyl-2-dimethylaminonaphthalene results in a pK decrease of 0·04 in each case. The electron-donating effect of the methyl group should result in an increase in the basicity of the substituted amine. All the basicity changes are small. Lack of additivity of the electronic

† σ^* is derived from rates of acid- and base-catalysed hydrolysis of 1-naphthoic acid esters between which are eliminated steric and resonance effects.[21] The σ value cited for 2-naphthyl is a mean of values derived from several " normal " reactions in which serious resonance effects are expected to be absent.[22] The value derived from dissociation of 2-naphthylamine (+0·12) is enhanced because of resonance stabilisation of 2-naphthylamine (*vide infra*) and is a σ^- value.[22]

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[22] A. Fischer, J. Packer, J. Vaughan, A. F. Wilson, and E. Wong, *J. Org. Chem.*, 1959, **24**, 155.
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[29] G. Thomson, *J.*, 1946, 1113.

effects of 4- and 5-substituents in 1-naphthoic acids has previously been observed [1] and Stone and Pearson [30] have noted the possible breakdown in the additivity relationship for polar effects of alkyl groups under severe steric compression, as here.

Acenaphthamines.—The 4- and 5-acenaphthenamines are stronger bases than the corresponding naphthylamines and dimethylaminonaphthalenes. More significantly, the acenaphthenamines are stronger bases than the corresponding 4,5-dimethylnaphthylamines and dimethylaminonaphthalenes. Thus 4-acenaphthenamine is 0·23 pK unit stronger than 4,5-dimethyl-2-naphthylamine and 4-dimethylaminoacenaphthene is 0·39 pK unit stronger than 4,5-dimethyl-2-dimethylaminonaphthalene. It was previously found that 4-acenaphthoic acid is weaker than 4,5-dimethyl-2-naphthoic acid ($\Delta pK = 0{\cdot}08$). These results suggest that the ethylene bridge is a more powerful electron donor than 4,5-dimethyl. The greater basicity of 5-acenaphthenamine and of 5-dimethylaminoacenaphthene, and lower acidity of 5-acenaphthoic acid, when compared with the analogous 4,5-dimethyl-1-naphthyl compounds, supports this conclusion.

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