The Remarkable Basicity of 1,8-Bis(dimethylamino)naphthalene

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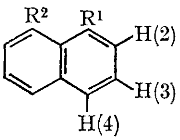
PERI-SUBSTITUTED NAPHTHALENES[1] provide a useful testing ground for steric effects and other interactions between substituents. We are interested in the interaction between non-bonding electron pairs and report here the first pK_a values for the 1,8-diaminonaphthalenes (I) to (IV). These, measured in water, are (I) 4·61; (II) 5·61; (III) 6·43; (IV) 12·34, and (IV) is thus stronger than normal *aliphatic* amines. The remarkable effect of the fourth methyl substituent is illustrated by the statement that ΔG at 25° in water for the reaction (III.H$^+$) + (IV) $\rightarrow$ (III) + (IV.H$^+$) will be -8 kcal. mole^{-1}.

The compounds (II), (III), and (IV) were prepared by alkylation of (I) with dimethyl sulphate: (IV), m.p. 47—48°, previously reported[2] as an oil, could be removed by extraction into an aqueous solution of pH 8, while (II), m.p. 103—104°, and (III), m.p. 29—30°, were separated by alumina chromatography. Compound (III) reacted readily with benzyl bromide to give (V), an oil. Analytical and full spectroscopic data in accord with the structures assigned were obtained for (II)—(V).

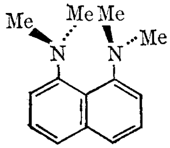
The n.m.r. spectrum of (IV) in CCl$_4$ shows a singlet at τ 7·29 (12H) and an ABX pattern (6H) which may be assigned to H(2) 3·24, H(3) 2·91, H(4) 2·82, J_{23} 7·6, J_{24} 1·2, J_{34} 7·9 Hz. In CF$_3$CO$_2$H the ABX pattern appears at lower field, H(2) τ 1·96, H(3) 2·29, H(4) 2·17, J_{23} 8·3, J_{24} 7·6, J_{34}

0·9 Hz, while the methyl protons appear as a doublet (J 2·0 Hz) at 6·79, split by the proton on nitrogen which appears at τ — 9·51 (1H). The long wavelength band in the u.v. spectrum (λ_{max} 335 mμ, log ϵ_{max} 3·96) shifts to 285 mμ (log ϵ_{max} 3·78) on protonation and similar shifts occur with (I), (II), and (III).

1,8-Bis(dimethylamino)naphthalene is clearly a strained molecule whose strains are very effectively relieved by protonation. Its conformation will reflect the interplay of several factors, *e.g.* steric inhibition of resonance, van der Waals repulsions and dipole–dipole repulsions, but a likely compromise (VI) with a lone-pair orbital/ring plane angle of 30—40° allows some n—π overlap as suggested by the u.v. and n.m.r. spectra. The n.m.r. spectrum of (V) is temperature dependent, coalescence of the AB quartet of the benzyl methylene group occurring at $-30°$. This implies a free energy of activation of about 12 kcal. mole^{-1} for rotation–inversion and a barrier of a similar order of magnitude is probable for (IV). By contrast with (IV) and (V), (III) has an intramolecular hydrogen bond (ν_{N-H} 3280 cm.$^{-1}$), and strain is not effectively relieved by protonation.



	R¹	R²
(I)	NH_2	NH_2
(II)	NHMe	NHMe
(III)	NMe_2	NHMe
(IV)	NMe_2	NMe_2
(V)	NMe·CH_2Ph	NMe_2



The second protonation of (IV) was followed by measuring the change in the chemical shift difference between the methyl groups of (IV) and those of the 1-naphthyldimethylammonium ion[3] as a function of sulphuric acid concentration. A good sigmoid curve was obtained with protonation half-complete in 86% H_2SO_4 ($H_0''' - 10·5$, though this scale[4] is not really applicable, H_+''' being appropriate). The mono-cation therefore has an autoprotolysis constant of about 10^{-20}, and the spectral parameters of the N–H · · · N bond are of interest. The extreme deshielding of the proton on nitrogen in the n.m.r. spectrum should be noted. The i.r. spectrum (CH_2Cl_2 and CH_2Br_2 solutions) of the monohydrobromide of (IV) shows no conventional N–H bonds, only a weak background absorption from about 3000 cm.$^{-1}$ to at least 800 cm.$^{-1}$, shifted to smaller wave numbers on deuteriation. Similar broad absorption has been observed[5] with strong intermolecular O–H · · · O and O–H · · · N bonds, but its origin is uncertain.

Finally (IV) might be expected to be only weakly nucleophilic for steric reasons. It may be recovered unchanged after 4 days at reflux with ethyl iodide in acetonitrile. It does react with methyl fluorosulphate but the solid product which separates is the fluorosulphonic acid salt of (IV).

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