Rates of Proton Transfer, Acid Dissociation Constants, and the Strengths of Intramolecular Hydrogen Bonds in 8-Methoxy-*NN*-dimethyl-1-naphthylammonium Ion and 8-Hydroxy-*NN*-dimethyl-1-naphthylamine

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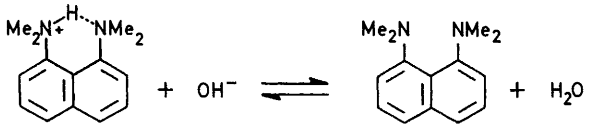
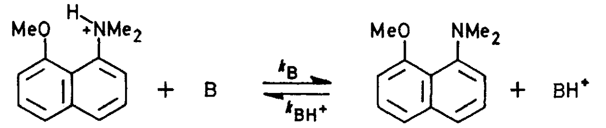
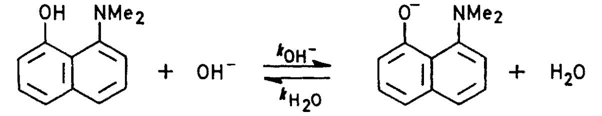
The rate coefficients for proton transfer from 8-hydroxy-*NN*-dimethyl-1-naphthylamine in 80% (v/v) dimethyl sulphoxide–water and from 8-methoxy-*NN*-dimethyl-1-naphthylammonium ion in aqueous solution are respectively 10^4 fold and 20—50 fold lower than expected for normal proton transfers from a hydroxy- and protonated amino-group. The low rates are due to intramolecular hydrogen bonds in the acids and by comparison with results for protonated 1,8-bis(dimethylamino)naphthalene, the rates show that in this series of *peri*-substituted naphthalenes the order of hydrogen bond strengths is $\overset{+}{N}$–H ··· O < O–H ··· N < $\overset{+}{N}$–H ··· N. The intramolecular hydrogen bonds also account for the unusual acidities; 8-methoxy-*NN*-dimethyl-1-naphthylammonium ion (p*K* 7.75) is a weaker acid by three p*K* units than *NN*-dimethyl-1-naphthylammonium ion and 8-hydroxy-*NN*-dimethyl-1-naphthylamine (p*K* *ca.* 14.9) is six p*K* units weaker than 1-naphthol.

THERMODYNAMICALLY favourable proton transfer from protonated 1,8-bis(dimethylamino)naphthalene to hydroxide ion [equation (1)] is exceptionally slow with a rate coefficient five orders of magnitude below the diffusion limited rate observed for other protonated amines.[1] For 1,8-bis(diethylamino)naphthalene, the rate coefficient is about two orders of magnitude lower still.[1b]


(1)


(2)


(3)

The factor most responsible for slow proton transfer is a strong intramolecular hydrogen bond in the protonated amines. A steric effect may also be involved. These results are of relevance in explaining the unusual basicity [2] of 1,8-bis(dimethylamino)naphthalene (proton sponge,[3] pK 12.3 [2]) which is considerably stronger than other aromatic amines, for example, *NN*-dimethyl-1-naphthylamine (pK *ca.* 4.9 [4]). It is likely that a considerable part of the enhanced basicity results from the strong intramolecular hydrogen bond which stabilises and lowers the acidity of the protonated amine. Other possible factors have been discussed.[2,5,6] For comparison with 1,8-bis(dimethylamino)naphthalene we have now carried out kinetic and equilibrium studies of proton transfer from 8-methoxy-*NN*-dimethyl-1-naphthylammonium ion to buffer species (B) in aqueous solution [equation (2)] and from 8-hydroxy-*NN*-dimethyl-1-naphthylamine to hydroxide ion in 80% (v/v) dimethyl sulphoxide–water [equation (3)].

EXPERIMENTAL

Materials.—Both 8-methoxy- and 8-hydroxy-*NN*-dimethyl-1-naphthylamine were prepared by methylation of 8-hydroxy-1-naphthylamine using dimethyl sulphate under different conditions. Fusion of the sodium salt of 8-aminonaphthalene-1-sulphonic acid with sodium and potassium hydroxides gave 8-hydroxy-1-naphthylamine [7] which was collected from the fusion mixture and treated with a 20 fold molar excess of dimethyl sulphate with stirring and cooling. In the preparation of 8-methoxy-*NN*-dimethyl-1-naphthylamine the mixture was maintained at pH >14 during the addition of dimethyl sulphate by adding 10M-sodium hydroxide while for 8-hydroxy-*NN*-dimethyl-1-naphthylamine the pH was kept at *ca.* 8—9. In both preparations after the addition of dimethyl sulphate, the the solutions were heated (steam-bath) for 2 h and the products were extracted into methylene chloride and distilled under reduced pressure. Crystals of 8-*methoxy*-NN-*dimethyl*-1-*naphthylamine*, m.p. 30°, were obtained (Found: C, 77.7; N, 7.0; H, 7.6. $C_{13}H_{15}NO$ requires C, 77.6; N, 7.0; H, 7.5%), $\delta(CCl_4)$ 2.88 (s, NMe_2), 4.00 (s, OMe), and 6.8—7.6 (m, aromatic). After distillation, 8-hydroxy-*NN*-dimethyl-1-naphthylamine was purified by recrystallisation from methanol to give a solid, m.p. 57—58°. The n.m.r. spectrum showed the sample to be at least 95% pure with <5% 8-methoxy-*NN*-dimethyl-1-naphthylamine as impurity (Found: C, 76.9; N, 7.4; H, 7.3. $C_{12}H_{13}NO$

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[1] F. Hibbert (*a*) *J.C.S. Chem. Comm.*, 1973, 463; (*b*) *J.C.S. Perkin II*, 1974, 1862.

[2] R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Comm.*, 1968, 723.

[3] Trade name given to 1,8-bis(dimethylamino)naphthalene by Aldrich Chemical Company.

[4] N. F. Hall and M. R. Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469; see also A. Fischer, G. J. Sutherland, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 1965, 5948.

[5] F. Hibbert in 'Chemical and Biological Applications of Relaxation Spectrometry,' ed. E. Wyn-Jones, Reidel, 1975, p. 387.

[6] F. Gerson, E. Haselbach, and G. Plattner, *Chem. Phys. Letters*, 1971, 316; E. Haselbach, A. Henriksson, F. Jachimowicz, and J. Wirz, *Helv. Chim. Acta*, 1972, **55**, 1757; M. R. Truter and B. L. Vickery, *J.C.S. Dalton*, 1972, 395; H. Einspahr, J.-B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Cryst.*, 1973, 1611.

[7] L. C. Raiford and E. P. Clark, *J. Amer. Chem. Soc.*, 1926, **48**, 483.

requires C, 77.0; N, 7.5; H, 7.0%), $\delta(CCl_4)$ 2.94 (s, NMe_2), 6.8—7.8 (m, aromatic), and 13.6 (s, OH).

p*K Measurements*.—8-*Methoxy*-NN-*dimethyl*-1-*naphthylamine*. Measurements of the equilibrium between 8-methoxy-*NN*-dimethyl-1-naphthylamine and the protonated amine were made spectrophotometrically in phosphate buffers at 25.0 °C. The buffers were made up in doubly distilled water and adjusted to ionic strength 0.1M with potassium chloride. The pH values were measured with a Pye Dynacap meter calibrated with borax [8] and hydrogen ion concentrations were calculated from $\log_{10}[H^+] = -pH + 0.122$.[9] Measurements of the extinction coefficients at 340 nm (ε_{app} = optical density/4 × stoicheiometric amine concentration) of solutions of the amine in 4 cm cells at various pH were used to obtain the ratio of protonated (RNH^+) to unprotonated (RN) amine, $[RNH^+]/[RN] = (\varepsilon_{RN} - \varepsilon_{app})/(\varepsilon_{app} - \varepsilon_{RNH^+})$. The calculated values for the acid dissociation constant of the protonated amine are shown in Table 1(a).

TABLE 1

Equilibrium measurements

(a) 8-methoxy-*NN*-dimethyl-1-naphthylamine						
pK = 7.75 ± 0.03, aqueous solution, ionic strength 0.1M, 25 °C						
$10^{-3}\varepsilon_{app}$/l mol^{-1} cm^{-1}	0.42	0.69	0.86	0.95	1.2	1.8
pH	6.87	7.20	7.31	7.43	7.60	7.89
10^8K/l mol^{-1}	2.1	1.8	1.8	1.7	1.6	1.6
$10^{-3}\varepsilon_{app}$/l mol^{-1} cm^{-1}	2.1	2.3	2.6			
pH	7.97	8.09	8.26			
10^8K/l mol^{-1}	1.9	1.8	1.8			
(b) 8-hydroxy-*NN*-dimethyl-1-naphthylamine						
Aqueous solution, pK = 14.9 ± 0.1, 25.5 °C						
$10^{-3}\varepsilon_{app}$/l mol^{-1} cm^{-1}	2.5	3.3	4.6	5.5	5.7	7.8
[KOH]/M	1.5	2.0	2.5	3.0	3.5	4.0
H_-[10]	14.33	14.51	14.69	14.85	15.00	15.15
$10^{15}K$/l mol^{-1}	0.9	1.0	1.2	1.2	0.9	1.2
$10^{-3}\varepsilon_{app}$/l mol^{-1} cm^{-1}	8.6	9.0				
[KOH]/M	4.5	5.0				
H_-[10]	15.28	15.44				
$10^{15}K$/l mol^{-1}	1.6	1.5				
80% (v/v) DMSO–H_2O $K' = (1.3 \pm 0.1) \times 10^2$, ionic strength 0.1M, 10 °C						
$10^{-3}\varepsilon_{app}$/l mol^{-1} cm^{-1}	1.4	2.7	3.1	4.7	5.6	5.8
10^3[NaOH]/M	1.0	2.0	2.5	4.0	5.0	6.0
$10^{-2}K'$/l mol^{-1}	1.1	1.3	1.2	1.4	1.5	1.3
$10^{-3}\varepsilon_{app}$/l mol^{-1} cm^{-1}	6.9	7.9	10.0			
10^3[NaOH]/M	8.0	10.0	25.0			
$10^{-2}K'$/l mol^{-1}	1.4	1.5	1.4			

8-*Hydroxy*-NN-*dimethyl*-1-*naphthylamine*. (i) Aqueous potassium hydroxide. Dissociation of the hydroxy-proton from 8-hydroxy-*NN*-dimethyl-1-naphthylamine [equation (3)] was measured spectrophotometrically at 350 nm in carbon dioxide free [10] potassium hydroxide solutions at 25.5 ±0.5 °C. The apparent extinction coefficients determined in potassium hydroxide solutions of varying concentrations were used to calculate the ratio [ROH] : [RO^-] for 8-hydroxy-*NN*-dimethyl-1-naphthylamine in the same way as described for 8-methoxy-*NN*-dimethyl-1-naphthylamine. Acid dissociation constants (K) shown in Table 1(b) were calculated using $pK = H_- + \log_{10}[ROH]/[RO^-]$ where H_- is the acidity function for these solutions measured using amine indicators.[10]

(ii) 80% Dimethyl sulphoxide–water (v/v). For comparison with kinetic results the equilibrium constant for reaction (3) was also measured at 10.0 and 25.0 °C in 80% DMSO–H_2O (v/v) containing sodium hydroxide and sufficient potassium chloride to maintain the ionic strength at 0.1M. The mixed solvent was made up by adding 80 parts by volume of DMSO to 20 parts by volume doubly distilled water. The degree of dissociation of 8-hydroxy-*NN*-dimethyl-1-naphthylamine in the presence of varying concentrations of sodium hydroxide was determined spectrophotometrically at 360 nm. The values obtained for the equilibrium constant (K') for reaction (3) in DMSO–water at 10.0 °C are shown in Table 1(b). The average value at 10.0 °C is $K' = 130 \pm 10$ compared with 106 ± 6 l mol^{-1} at 25.0 °C.

A H_- acidity function has been measured for DMSO–H_2O mixtures containing 0.011M-tetramethylammonium hydroxide.[11] Assuming that the same acidity function applies under the present conditions a pK value of 17.4 was calculated for 8-hydroxy-*NN*-dimethyl-1-naphthylamine. This is in poor agreement with the value determined in aqueous potassium hydroxide solutions, pK = 14.9 ± 0.1. This latter result is considered to be more reliable since the acidity function used to calculate a value for DMSO–H_2O probably does not apply exactly under our experimental conditions.

Kinetic Measurements.—Kinetic results for reactions (2) and (3) were obtained using the temperature-jump instrument manufactured by Messanlagen Studiengesellschaft, Göttingen. For 8-methoxy-*NN*-dimethyl-1-naphthylamine a 40 kV discharge from a 0.05 μF capacitor was used to heat 2.0 ml of an aqueous solution from 20.2 to 25.0 °C. The heating time which is <15 μs under these conditions was measured for a solution of Phenol Red in a tris(hydroxymethyl)aminomethane buffer at ionic strength 0.1M. For 8-hydroxy-*NN*-dimethyl-1-naphthylamine a 15 kV discharge from a 0.01 μF capacitor raised the temperature of 0.44 ml of an 80% DMSO–H_2O solution from 9.0 to 10.0 °C. Under these conditions the heating time measured with a solution of 4-nitrodiphenylamine in 80% DMSO–H_2O containing 0.001M-sodium hydroxide and with an ionic strength 0.1M was <20 μs. The temperatures of the thermostatted reaction solutions were measured before temperature-jump by means of a thermocouple. The chemical relaxations which occurred after the temperature rise were observed at $\lambda_{max.}$ for the basic forms and relaxation times (τ) were calculated as previously described.[1b]

RESULTS

8-*Methoxy*-NN-*dimethyl*-1-*naphthylamine*.—Attempts to study the kinetics of reaction (2) with $B = OH^-$ for aqueous solutions of 8-methoxy-*NN*-dimethyl-1-naphthylamine at pH 7—8 containing Phenol Red as indicator were unsuccessful because it could not be established with certainty that the relaxation which was observed under these conditions referred to reaction (2).[12] Reliable results were obtained for reaction (2) with B as monohydrogen orthophosphate dianion, tris(hydroxymethyl)aminomethane, and 2-amino-2-methylpropane-1,3-diol and BH^+ as the corresponding protonated forms. Chemical relaxations were

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[8] R. G. Bates, 'Determination of pH,' Wiley, New York, 1964, p. 123.

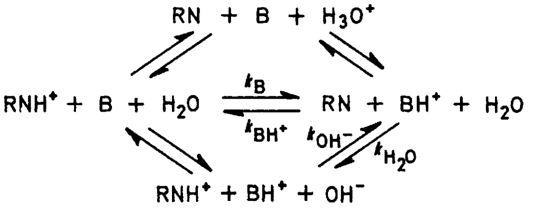
[9] Ref. 8, p. 92.

[10] G. Yagil, *J. Phys. Chem.*, 1967, **71**, 1034.

[11] D. Dolman and R. Stewart, *Canad. J. Chem.*, 1967, **45**, 911.

[12] M. H. Miles, E. M. Eyring, W. W. Epstein, and R. E. Ostlund, *J. Phys. Chem.*, 1965, **69**, 467.

observed with 8-methoxy-*NN*-dimethyl-1-naphthylamine (RN) in these buffer solutions (pH 7.2—8.6) at 25.0 °C and ionic strength 0.1M. In these solutions process (4) applies.[13]



(4)

Under conditions with OH^- buffered and with buffer in at least 10-fold excess over 8-methoxy-*NN*-dimethyl-1-naphthylamine {for example for a 3 : 1 tris(hydroxymethyl)-aminomethane buffer $[RN] + [RNH^+] = 4 \times 10^{-5}$ and $[B] + [BH^+] = 1-14 \times 10^{-3}$M, pH = 7.8}, the only observable relaxation time is given by (5) where $r = [B]/[BH^+]$.[13,14] Results for the variation of reciprocal relaxation time with buffer concentration in tris(hydroxymethyl)-aminomethane buffers with buffer ratios $r = 1.0$ and 0.33 are shown in Figure 1. The intercept is given by the first two terms in expression (5) but the results are not sufficiently precise to permit accurate calculation of k_{OH^-} (k_{OH^-} *ca.* 10^9 l mol^{-1} s^{-1}). Values of k_B and k_{BH^+} calculated from the gradients of the plots are shown in Table 2. The ratio

$$1/\tau = k_{OH^-}[OH^-] + k_{H_2O}[H_2O] + (k_B r + k_{BH^+})[BH^+] \quad (5)$$

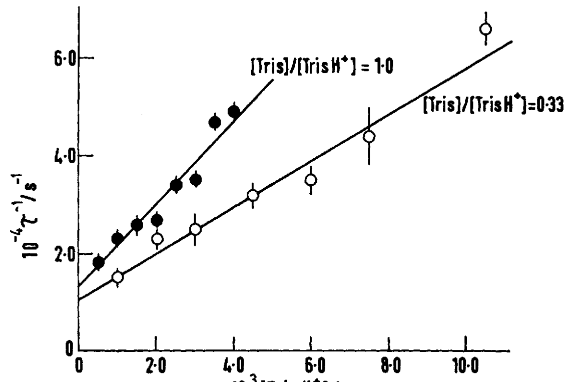


FIGURE 1 Dependence of reciprocal relaxation time on buffer concentration for 8-methoxy-*NN*-dimethyl-1-naphthylammonium ion in tris(hydroxymethyl)aminomethane buffers

TABLE 2

Forward (k_B) and reverse (k_{BH^+}) rate coefficients for proton transfer from 8-methoxy-*NN*-dimethyl-1-naphthylammonium ion to buffer bases (B) in aqueous solution *

B	pK_{BH^+}	$10^{-7}k_B$/l mol^{-1} s^{-1}	$10^{-7}k_{BH^+}$/l mol^{-1} s^{-1}
HPO_4^{2-}	6.74	0.4 ± 0.2	2.8 ± 0.5
$(HOCH_2)_3CNH_2$	8.08	0.6 ± 0.1	0.3 ± 0.1
$(HOCH_2)_2C(Me)NH_2$	8.80	1.8 ± 0.2	0.16 ± 0.03

* 25.0 °C, ionic strength 0.1M.

$k_B : k_{BH^+} = 2 \pm 1$ is within experimental error of the equilibrium constant (2.1 ± 0.4) calculated from the p*K* values of tris(hydroxymethyl)aminomethane and 8-methoxy-*NN*-dimethyl-1-naphthylamine. The kinetic results in phosphate buffers were treated in the same way and the ratio of rate coefficients $k_B : k_{BH^+}$ was again compatible with the equilibrium constant obtained from p*K* values. For 2-amino-2-methylpropane-1,3-diol a value for k_B, only, was obtained from measurements at two buffer ratios since the term involving k_{BH^+} makes a small contribution. The value of k_{BH^+} was calculated by combining the measured value of k_B with the equilibrium constant.

8-Hydroxy-NN-*dimethyl*-1-*naphthylamine*.— Chemical relaxations for equilibrium (3) could not be observed in concentrated aqueous potassium hydroxide solutions.

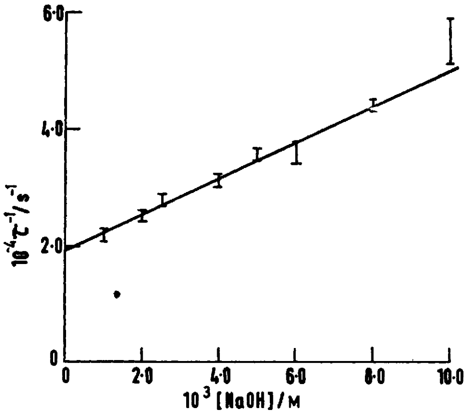


FIGURE 2 Dependence of reciprocal relaxation time on hydroxide ion concentration for 8-hydroxy-*NN*-dimethyl-1-naphthylamine in 80% (v/v) DMSO–H_2O

Measurements were made at 10.0 °C in 80% (v/v) DMSO–H_2O containing sodium hydroxide (0.001—0.02M) and enough potassium chloride to keep the ionic strength at 0.1M. With hydroxide ion concentrations in at least five-fold excess over 8-hydroxy-*NN*-dimethyl-1-naphthylamine the reciprocal relaxation time for (3) is given by (6).

$$1/\tau = k_{OH^-}[OH^-] + k_{H_2O}[H_2O] \quad (6)$$

The variation of reciprocal relaxation time with hydroxide ion concentration is shown in Figure 2 and the calculated rate coefficients k_{OH^-} and $k_{H_2O}[H_2O]$ are shown in Table 3.

TABLE 3

Forward (k_{OH^-}) and reverse (k_{H_2O}) rate coefficients for proton transfer from 8-hydroxy-*NN*-dimethyl-1-naphthylamine to hydroxide ion in 80% (v/v) DMSO–H_2O [a]

$10^{-6}k_{OH^-}$/ l mol^{-1} s^{-1}	$10^{-4}k_{H_2O}[H_2O]$/ s^{-1}	$10^{-2}k_{OH^-}$/ $k_{H_2O}[H_2O]$	$10^{-2}K'$/ l mol^{-1}
3.0 ± 0.3	2.0 ± 0.2	1.5 ± 0.3	1.3 ± 0.1

[a] 10.0 °C, ionic strength 0.1M.

The ratio of rate coefficients $k_{OH^-}/k_{H_2O}[H_2O] = 150 \pm 30$ is in reasonable agreement with the separately measured equilibrium constant $K' = 130 \pm 10$ l mol^{-1}.

For equilibrium (3) under conditions where hydroxide ion is in excess, the change in intensity of transmitted light ($\delta I/I$) which results from the decrease in concentration of

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[13] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1; M. Eigen and L. de Maeyer, ' Technique of Organic Chemistry,' eds. S. L. Friess, E. S. Lewis, and A. Weissberger, Interscience, New York, 1963, vol. VIII, part 2, p. 895.

[14] C. F. Bernasconi, *J. Phys. Chem.*, 1971, **75**, 3636.

the anion of 8-hydroxy-*NN*-dimethyl-1-naphthylamine occurring in the chemical relaxation, is given [15] by equation (7). In equation (7) ΔT represents the size of the temperature jump (1.0°), ΔH° is the heat of reaction, and $\varepsilon_{\mathrm{RO}^-}$ is the extinction coefficient of the anion. Equation (7)

$$\delta I/I = -2.3(\Delta T)(\Delta H^\circ)\varepsilon_{\mathrm{RO}^-}[\mathrm{ROH}]_{\mathrm{st}}K'[\mathrm{OH}^-]/R(T - \Delta T)T(1 + K'[\mathrm{OH}^-])^2 \quad (7)$$

predicts that the amplitude of the relaxation ($\delta I/I$) measured for a fixed total concentration of 8-hydroxy-*NN*-dimethyl-1-naphthylamine ($[\mathrm{ROH}]_{\mathrm{st}}$) will go through a maximum as $[\mathrm{OH}^-]$ is varied which will occur when $[\mathrm{OH}^-] = 1/K'$. Experimental values showed this behaviour with a maximum at $[\mathrm{OH}^-] = 0.006 \pm 0.001\mathrm{M}$ which leads to an equilibrium constant [$K' = (1.7 \pm 0.3) \times 10^2$ l mol^{-1} at 10.0 °C] in fair agreement with the values in Table 3 obtained from kinetic and equilibrium measurements. Reasonable agreement was also observed between the value of the heat of reaction (ΔH° -2.9 ± 0.2 kcal mol^{-1}) calculated from equation (7) and the value (ΔH° -2.6 ± 1.5 kcal mol^{-1}) calculated from the equilibrium constants at 10.0 and 25.0 °C.

DISCUSSION

The results in Tables 2 and 3 will be used to show that proton transfers involving 8-methoxy-*NN*-dimethyl-1-naphthylamine and 8-hydroxy-*NN*-dimethyl-1-naphthylamine are slower than observed for most oxygen or nitrogen acids. However the effects are not so dramatic as found for 1,8-bis(dimethylamino)naphthalene.[1] Thermodynamically favourable proton transfers for most oxygen and nitrogen acids in aqueous solution occur with rate coefficients which are close to the diffusion limit (normal proton transfer).[13] Much lower rates are observed if the acidic proton is held in an intramolecular hydrogen bond and this is the reason for the low rates observed here. By making reasonable assumptions about the mechanism of proton transfer it can be shown that for a thermodynamically favourable proton transfer from a hydrogen bonded acid, the amount by which the rate coefficient is lower than the diffusion limit gives the value of the equilibrium constant between hydrogen bonded and non-hydrogen bonded forms of the acid.[1b,16,17]

The results in Table 2 for proton transfer between 8-methoxy-*NN*-dimethyl-1-naphthylammonium ion and buffers refer to reactions where the acid–base pairs have roughly equal acidity and the reactions are not strongly thermodynamically favourable in either direction. The rate coefficients for proton removal by phosphate, tris(hydroxymethyl)aminomethane, and 2-amino-2-methylpropane-1,3-diol increase as the buffer is made more strongly basic. For reaction with tris(hydroxymethyl)aminomethane where the p*K* values for the two acid–base pairs are very similar the rate coefficient k_{B} has the value $(6 \pm 1) \times 10^6$ l mol^{-1} s^{-1} compared for example with the rate coefficient *ca.* 3×10^8 l mol^{-1} s^{-1} observed for normal proton transfer between trimethylammonium ion and trimethylamine.[18] The other rate coefficients in Table 2 are roughly 20—50 fold lower than the rates observed for acids and bases showing normal proton transfer behaviour and with p*K* values similar to those for the acids and bases in Table 2. The results show that 8-methoxy-*NN*-dimethyl-1-naphthylammonium ion is weakly intramolecularly hydrogen bonded with an equilibrium constant for hydrogen bond breakage to give the non-hydrogen bonded form of the acid of *ca.* $2—5 \times 10^{-2}$.

The thermodynamically favourable proton transfer from 8-hydroxy-*NN*-dimethyl-1-naphthylamine to hydroxide ion [equation (3)] in 80% (v/v) DMSO–H_2O at 10.0 °C occurs with a rate coefficient 3×10^6 l mol^{-1} s^{-1} compared with the result [13] *ca.* 1×10^{10} l mol^{-1} s^{-1} which is observed for normal proton transfer from an oxygen acid in aqueous solution at 10 °C. The diffusion limit in the mixed solvent will be almost the same as in water.[19] The equilibrium constant for breakage of the intramolecular hydrogen bond in 8-hydroxy-*NN*-dimethyl-1-naphthylamine to give the non-hydrogen bonded acid is therefore *ca.* 3×10^{-4} in 80% DMSO–H_2O. For protonated 1,8-bis(dimethylamino)naphthalene the rate coefficient measured [1] for proton removal by hydroxide ion in aqueous solution was 1.9×10^5 l mol^{-1} s^{-1}. In this case the equilibrium constant for breakage of the $\overset{+}{\mathrm{N}}\text{–H} \cdots \mathrm{N}$ hydrogen bond is *ca.* 1×10^{-5}. Therefore, based on the rates of proton transfer, the order of strengths of the intramolecular hydrogen bonds in these three *peri*-substituted naphthalenes is $\overset{+}{\mathrm{N}}\text{–H} \cdots \mathrm{O} < \mathrm{O}\text{–H} \cdots \mathrm{N} < \overset{+}{\mathrm{N}}\text{–H} \cdots \mathrm{N}$.

Some evidence for the presence of a moderately strong intramolecular hydrogen bond in 8-hydroxy-*NN*-dimethyl-1-naphthylamine in non-aqueous solvents is provided by spectroscopic data. The sharp absorbance at 3 610 cm^{-1} due to the OH stretching vibration in 1-naphthol [20] (0.02M solution in CCl_4) is missing from the spectrum of 8-hydroxy-*NN*-dimethyl-1-naphthylamine and is replaced by a broad absorbance around 2 400—3 300 cm^{-1} (0.02M solution in CCl_4). The hydroxy-proton resonance in the n.m.r. spectrum of 8-hydroxy-*NN*-dimethyl-1-naphthylamine in $CDCl_3$ occurs at δ 13.6 compared with 5.15 for 1-naphthol. The extent of downfield shift of the proton resonance of a hydroxy-group involved in a hydrogen bond compared with a non-hydrogen bonded hydroxy is thought [21] to reflect the strength of the hydrogen bond. The fairly large shift in this case signifies a moderately strong bond. For 8-methoxy-1-naphthol the hydroxy-resonance occurs [22] at

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[15] E. F. Caldin, *Chem. in Britain*, 1975, **11**, 4.

[16] R. P. Jensen, E. M. Eyring, and W. M. Walsh, *J. Phys. Chem.*, 1966, **70**, 2264.

[17] M. Eigen, W. Kruse, G. Maass, and L. de Maeyer, *Progr. Reaction Kinetics*, 1964, **2**, 285.

[18] E. Grunwald and M. Cocivera, *Discuss Faraday Soc.*, 1965, **39**, 105.

[19] C. F. Bernasconi and F. Terrier, *J. Amer. Chem. Soc.*, 1975, **97**, 7458.

[20] L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' Methuen, London, 2nd edn., 1958, p. 95.

[21] A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, *J. Amer. Chem. Soc.*, 1960, **82**, 5057; J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1965, p. 546.

[22] A. G. Brown, J. C. Lovie, and R. H. Thomson, *J. Chem. Soc.*, 1965, 2355.

δ 9.28 which probably means that the hydrogen bond is fairly weak. The i.r. spectrum [22] in CCl_4 confirms this.

Acids in which the dissociating proton is involved in an intramolecular hydrogen bond often have abnormally high p*K*,[23] and the results obtained with *peri*-substituted naphthalenes confirm this. The decreased acidity should correspond to the logarithm of the equilibrium constant between hydrogen bonded and non-hydrogen bonded forms of the acid. The p*K* of 8-methoxy-*NN*-dimethyl-1-naphthylamine is about three orders of magnitude higher than p*K* = 4.9 observed [4] for *NN*-dimethyl-1-naphthylamine. This difference is not solely attributable to the hydrogen bond since there will be other effects on introducing a methoxy-substituent, but it is probable that the effect of the intramolecular hydrogen bond is quite small. The effect for 8-hydroxy-*NN*-dimethyl-1-naphthylamine is larger, in accord with the stronger hydrogen bond for this compound, and the p*K* is about six units higher than measured for 1-naphthol (p*K* 9.3).[24] For 1,8-bis(dimethylamino)naphthalene the p*K* value [2] (12.3) is seven units higher than that of *NN*-dimethyl-1-naphthylamine. The intramolecular hydrogen bond in this protonated amine probably makes a large contribution to the enhanced p*K*. There are other *peri*-substituted naphthalenes in which intramolecular hydrogen bonding modifies the acid–base behaviour. For example, dissociation of the second proton from 4,5-dihydroxynaphthalene-2,7-disulphonic acid [25] occurs with p*K* *ca.* 15.8 as a result of a strong $O\text{-}H \cdots \bar{O}$ hydrogen bond in the monoanion. The u.v. spectrum of 8-methoxy-1-naphthol is unchanged by the addition of alkali [26] which is taken to mean that the acidity relative to that of 1-naphthol is weakened by an intramolecular hydrogen bond. However the hydroxy-group in 4-amino-5-hydroxynaphthalene-2,7-disulphonic acid has p*K* 8.8 [27] which is very similar to that for 1-naphthol. This arises because both the acid and its anion can be stabilised by hydrogen bonds.

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