Temperature-jump Study of Proton Transfer from Protonated 1,8-Bis(dialkylamino)naphthalenes to Hydroxide Ion in Water and Aqueous Dioxan

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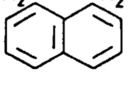
The rate coefficients for proton transfer from the protonated forms of 1,8-bis(dimethylamino)- (I) and 1,8-bis-(diethylamino)-naphthalene (II) to hydroxide ion have been determined using the temperature-jump technique. For (I) in aqueous solution, the rate is five orders of magnitude below the diffusion limited rate expected for thermodynamically favourable proton transfer from a nitrogen acid. In 20% dioxan–water (v/v), the rate for (II) is *ca.* 10^2 times lower than for (I). Proton transfers involving (I) and (II) occur slowly largely because of a strong intramolecular hydrogen bond in the protonated amines. Steric strain in the transition states may also contribute and is partly responsible for the large rate difference observed for (I) and (II).

THERMODYNAMICALLY favourable proton transfer from nitrogen or oxygen acids usually occurs at a rate which is diffusion controlled.[1] There are a limited number of proton transfers, however, where the rate is below the diffusion limited value.[1] These exceptions are of particular interest and we now report an example of one such reaction: proton transfer (1) between hydroxide

$$BH^+ + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B + H_2O \qquad (1)$$

ion and the conjugate acids of 1,8-bis(dimethylamino)- and 1,8-bis(diethylamino)-naphthalenes.



(I) R = Me
(II) R = Et
(III) R = H

Compound (I) is an exceptionally strong base [2] having a pK_a even higher than that of an aliphatic amine. The molecule is strained [3] and the relief of strain which occurs on protonation is thought [2] to contribute to the high pK_a. The protonated amine possesses an intramolecular hydrogen bond [4] and this may also be important. It is of interest to examine the consequences of these factors on the rate of proton transfer. A preliminary account of this work has been published.[5]

EXPERIMENTAL

Materials.—Commercial samples of 1,8-bis(dimethylamino)- (I) and 1,8-diamino-naphthalene (III) were recrystallised from ethanol and from 30% ethanol–water respectively. 1,8-Bis(diethylamino)naphthalene (II) was prepared by a method described to us by Dr. R. W. Alder in which (III), purified by Soxhlet extraction with light petroleum, b.p. 40—60°, was alkylated using diethyl sulphate. The product was extracted into an aqueous solution of pH *ca.* 9 and then precipitated by adding base. Extraction with methylene chloride, followed by distillation under reduced pressure and recrystallisation from methanol gave a solid, m.p. 28°, with satisfactory n.m.r. spectrum and analysis figures.

Buffer solutions were made up in doubly distilled water using carbon dioxide-free sodium hydroxide solutions which had been standardised against potassium hydrogen phthalate. Potassium chloride and disodium hydrogen orthophosphate were dried before use. AnalaR dioxan was refluxed over sodium and distilled.

*p*K *Measurements.*—Equilibrium constants (K) for reaction (1) at 25·0° and ionic strength $I = 0{\cdot}1\text{M}$ were determined for (I) in aqueous solution and for (I) and (II) in 20% dioxan–water (v/v). A solution of the amine in dioxan (0·01 ml) was injected from a calibrated Hamilton syringe into stirred sodium hydroxide solutions (10 ml) of different molarity. Measurements of the apparent extinction coefficient of the amine (ε_{app} measured optical density/stoicheiometric amine concentration) were made at 345 nm in 40 mm cells using a Unicam SP 500 spectrophotometer with a thermostatted cell-holder. At 345 nm, the free amines absorb strongly but the protonated amines have negligible absorbance. In aqueous solution the low solubilities of the amines meant working with very dilute solutions [*ca.* 1×10^{-5} and $3 \times 10^{-6}\text{M}$ for (I) and (II) respectively] having low optical densities. Only a very rough value could be obtained for (II) in aqueous solution. The problem was partly overcome by using 20% dioxan–water (v/v) as solvent in which concentrations for (I) of 2×10^{-5} and for (II) of $1 \times 10^{-5}\text{M}$ were used.

Plots of ε_{app} against $\varepsilon_{app}/[OH^-]$ were linear as required by $\varepsilon_{app} = \varepsilon_B - ([H_2O]/K)\varepsilon_{app}/[OH^-]$ where ε_B is the extinction coefficient of the free amine. Values for K were calculated using a least-squares analysis and combined with the ionic product of water to give pK_a values for the amines at an

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[1] (*a*) M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1; (*b*) M. Eigen, W. Kruse, G. Maass, and L. de Maeyer, *Progr. Reaction Kinetics*, 1964, **2**, 285.

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

[3] H. Einspahr, J.-B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Cryst.*, 1973, 1611.

[4] M. R. Truter and B. L. Vickery, *J.C.S. Dalton*, 1972, 395.

[5] F. Hibbert, *J.C.S. Chem. Comm.*, 1973, 463.

ionic strength of 0·1M ($\mathrm{p}K_a^{0\cdot1}$). The ionic product of water in 20% dioxan–water (v/v) at I 0·1M was calculated from the value at $I = 0$ in this solvent [6] using $\mathrm{p}K_w^{0\cdot1} = \mathrm{p}K_w^{0} - AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ where $A = 0\cdot744$.[6]

Kinetic Measurements.—Relaxation times for equation (1) were determined at 24·6° using the temperature-jump apparatus manufactured by Messanlagen Studiengesellschaft, Göttingen. A 40 kV discharge from a 0·05 μF capacitor raised the temperature of a solution thermostatted at 19·8 by 4·8° within 2—3 μs. The temperature change was calculated from the energy stored in the capacitor and the volume (2 ml) of the heated solution. The magnitude of the temperature jump was also determined experimentally by observing the change in optical density at 460 nm of a solution containing ferric nitrate (*ca.* 0·002M), potassium thiocyanate (*ca.* 0·002M), and sulphuric acid (*ca.* 0·1M) after a discharge of 40 kV. From a calibration curve of optical density against temperature, obtained using a Unicam SP 500 spectrophotometer, the temperature rise was calculated as 4·5 ± 0·5°.

Chemical relaxations of equilibrium (1) were observed by following the increase in optical density at 335 nm due to an increase in concentration of the amine B. Where possible, observations were also made at 285 nm of the decrease in optical density due to the decrease in concentration of $\mathrm{BH^+}$. For (I), reaction solutions consisted of phosphate or trifluoroethanol buffers saturated with the amine. Phosphate buffers were made up according to Bates [7] and trifluoroethanol buffers were prepared by mixing weighed amounts of the alcohol with 0·1M-sodium hydroxide. The pH values were calculated from $[\mathrm{CF_3CH_2O^-}]/[\mathrm{CF_3CH_2OH}][\mathrm{OH^-}] = 40\cdot7$.[8] The calculated values agreed to within 0·04 (average deviation) of values measured at 25° using a glass electrode (Electronic Instruments 1070). Traces of the change in optical density with time after the temperature jump were displayed on a Tektronix 549 oscilloscope, photographed, and projected onto graph paper. The results were plotted in the form $\log_{10}(D_\infty - D_t)$ against time where D_∞ and D_t are the optical densities after complete reaction and after time t respectively. The plots were linear for at least two-half-lives. Relaxation times were usually reproducible to better than ±10% (average deviation) and the mean of at least five determinations was calculated.

RESULTS

Acid Dissociation Constants.—Equilibrium constants (K) and $\mathrm{p}K_a^{0\cdot1}$ values for (I) in water and for (I) and (II) in 20% dioxan–water (v/v) are shown in Table 1. For (I), $\mathrm{p}K_a^{0\cdot1}$ in water is within experimental error of the previous determination,[2,9] and the difference between the values in water and dioxan–water is about the same as observed for other amines.[10] The increased $\mathrm{p}K_a^{0\cdot1}$ of (II) compared with (I) is similar to the pK difference between *NN*-dimethyl- and *NN*-diethyl-aniline and between trimethyl- and triethylamine.[11] Hence replacement of the methyl groups in (I) by ethyl does not lead to a substantial increase in strain.

Proton Transfer for 1,8-*Bis*(*dimethylamino*)*naphthalene in Aqueous Solution.*—*Relaxation times.* Evidence will be presented below which shows that the observed chemical relaxations refer to equilibrium (1) in which k_f and k_r are the forward and reverse second-order rate coefficients respectively. Relaxation times (τ) were determined in trifluoroethanol buffers with pH values between 11·3 and 12·4. The relaxation times shown in Table 2(a) were independent of the concentration of amine and at a fixed pH were independent of buffer concentration. The dependence of reciprocal relaxation time upon hydroxide ion concentration shown in Figure 1 and equation (2) is of the expected form. The

$$1/\tau = k_r[\mathrm{H_2O}] + k_f[\mathrm{OH^-}] \qquad (2)$$

TABLE 1

(A) Dissociation of 1,8-bis(dimethylamino)naphthalene at I = 0·1M and 25°

(a) Aqueous solution

$K = [\mathrm{B}][\mathrm{H_2O}]/[\mathrm{BH^+}][\mathrm{OH^-}] = 2\cdot9 \pm 0\cdot7 \times 10^3$; $\mathrm{p}K_a^{0\cdot1} = 12\cdot1 \pm 0\cdot1$

NaOH/M	0·98	0·098	0·049	0·0392	0·0294
$10^{-3}\,\varepsilon_{\mathrm{app}}$	7·0	6·3	5·5	4·8	4·0
NaOH/M	0·0196	0·0098	0·00785	0·00393	0·00196
$10^{-3}\,\varepsilon_{\mathrm{app}}$	3·8	2·5	2·3	0·93	0·73

(b) 20% Dioxan–water (v/v)

$K/[\mathrm{H_2O}] = 630 \pm 50$; $\mathrm{p}K_a^{0\cdot1} = 11\cdot5 \pm 0\cdot2$

NaOH/M	0·100	0·050	0·020	0·010	0·0060
$10^{-3}\varepsilon_{\mathrm{app}}$	8·9	8·7	8·3	7·9	7·2
NaOH/M	0·0040	0·0030	0·0020	0·0010	0·00050
$10^{-3}\,\varepsilon_{\mathrm{app}}$	6·6	6·1	5·2	3·5	2·1

(B) Dissociation of 1,8-bis(diethylamino)naphthalene in 20% dioxan–water (v/v) at I = 0·1M and 25°

$K/[\mathrm{H_2O}] = 40 \pm 8$; $\mathrm{p}K_a^{0\cdot1} = 12\cdot7 \pm 0\cdot2$

NaOH/M	0·100	0·050	0·030	0·020	0·010
$10^{-3}\varepsilon_{\mathrm{app}}$	6·8	5·5	4·8	3·9	2·5
NaOH/M	0·0060	0·0050			
$10^{-3}\,\varepsilon_{\mathrm{app}}$	1·6	1·5			

TABLE 2 *

(a) Proton transfer for 1,8-bis(dimethylamino)naphthalene in aqueous solution at 24·6°

$\mathrm{CF_3CH_2OH–CF_3CH_2O^-}$ Buffers (I 0·1M)

$[\mathrm{OH^-}]$/M	0·0034	0·0047	0·0072	0·0170	0·0210
pH	11·30	11·44	11·63	12·00	12·09
$10^{-3}\tau^{-1}/\mathrm{s^{-1}}$	4·4 ± 0·3	5·1 ± 0·2	4·4 ± 0·3	5·7 ± 0·5	7·0 ± 0·4
$[\mathrm{OH^-}]$/M	0·0232	0·0295	0·0320	0·0410	
pH	12·14	12·24	12·28	12·38	
$10^{-3}\tau^{-1}/\mathrm{s^{-1}}$	9·0 ± 0·4	10·5 ± 1·0	11·7 ± 1·0	11·7 ± 1·0	

$\mathrm{HPO_4^{2-}–PO_4^{3-}}$ Buffers (I 0·10 ± 0·01M)

pH	10·90	11·10	11·30	11·50	11·70
$10^{-3}\tau^{-1}/\mathrm{s^{-1}}$	3·9 ± 0·2	4·2 ± 0·7	3·9 ± 0·4	3·9 ± 0·6	3·9 ± 0·7

$\mathrm{DPO_4^{2-}–PO_4^{3-}}$ Buffers in $\mathrm{D_2O}$ (I 0·10 ± 0·01M)

pD	10·91	11·51
$10^{-3}\tau^{-1}/\mathrm{s^{-1}}$	1·46 ± 0·06	1·61 ± 0·08

(b) Proton transfer in 20% dioxan–water (v/v) containing $\mathrm{HPO_4^{2-}–PO_4^{3-}}$ buffers

Stoicheiometric buffer ratio $[\mathrm{HPO_4^{2-}}]:[\mathrm{PO_4^{3-}}]$	11·0	3·0	0·25
1,8-Bis(dimethylamino)-naphthalene $10^{-3}\,\tau^{-1}/\mathrm{s^{-1}}$	0·73 ±0·06	0·88 ±0·05	2·3 ±0·2
1,8-Bis(diethylamino)-naphthalene $10^{-3}\,\tau^{-1}/\mathrm{s^{-1}}$	0·116 ±0·07	0·109 ±0·006	0·119 ±0·008

* Uncertainties are ± average deviation.

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[6] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' Rheinhold, New York, 1958, 3rd edn., pp. 713, 756.

[7] R. G. Bates, 'Determination of pH,' Wiley, New York, 1964, p. 162.

[8] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1959, **81**, 1050.

[9] R. W. Alder, personal communication.

[10] J. C. James and J. G. Knox, *Trans. Faraday Soc.*, 1950, **46**, 254; H. P. Marshall and E. Grunwald, *J. Amer. Chem. Soc.*, 1954, **76**, 2000.

[11] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965; supplement, 1972.

observed values for k_f and k_r were $1·9 \pm 0·4 \times 10^5$ and 70 ± 10 l mol^{-1} s^{-1} respectively. The ratio $k_f : k_r = 2·7 \pm 0·8 \times 10^3$ is in good agreement with the separately measured equilibrium constant $K = 2·9 \pm 0·7 \times 10^3$ (Table 1).

In phosphate buffers (pH 10·9—11·7), the relaxation time is approximately independent of pH ($1/\tau = 4·0 \pm 0·5 \times 10^3$ s^{-1}) [see Table 2(a)]. Over this pH range, the reverse reaction which corresponds to the first term in equation (2) makes a much larger contribution than the forward reaction. A value of $k_r = 72 \pm 9$ l mol^{-1} s^{-1} is calculated, in good agreement with the result in trifluoroethanol buffers. From similar experiments in D_2O, k_r 27 ± 2 l mol^{-1} s^{-1} is obtained giving an isotope effect $k_r(H_2O) : k_r(D_2O) = 2·7 \pm 0·5$.

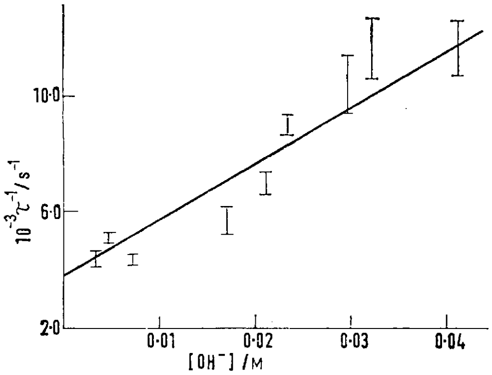


FIGURE 1 Variation of reciprocal relaxation time with hydroxide ion concentration for 1,8-bis(dimethylamino)naphthalene in trifluoroethanol buffers

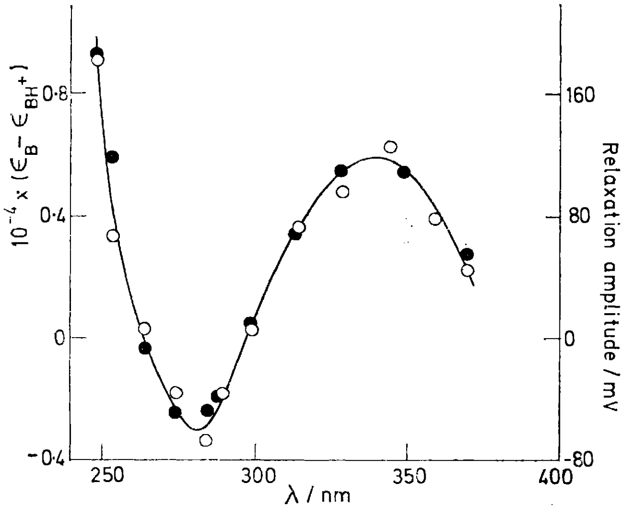


FIGURE 2 Dependence of relaxation amplitude (●, right scale) and extinction coefficient difference $\times 10^{-4}$ ($\varepsilon_B - \varepsilon_{BH^+}$) (○, left scale) upon wavelength for 1,8-bis(dimethylamino)naphthalene

Relaxation amplitude. An increase in temperature disturbs equilibrium (1) in the direction of products. The amplitude of the relaxation as measured by the change in optical density following the temperature jump should be identical with the value of $\Delta c(\varepsilon_B - \varepsilon_{BH^+})$ where Δc is the increase in concentration of B (or decrease in BH^+) and ε_B and ε_{BH^+} are the extinction coefficients of B and BH^+ at the wavelength of observation. This is confirmed by the results shown in Figure 2 for the variation of relaxation amplitude (10 mV signal is equivalent to an optical density change of 0·001) and extinction coefficient difference ($\varepsilon_B - \varepsilon_{BH^+}$) with wavelength.

Proton Transfer for 1,8-*Bis*(*dimethylamino*)- *and* 1,8-*Bis*-(*diethylamino*)-*naphthalenes in* 20% *Dioxan–Water* (*v*/*v*).—The low solubility of (II) meant that no relaxation was observable in aqueous solutions containing (II) under our experimental conditions. However relaxations were observable for both (I) and (II) in 20% dioxan–water (v/v). Relaxation times determined at three different phosphate buffer ratios are shown in Table 2(b). The results permit a comparison of rates for (I) and (II) despite the fact that hydroxide ion concentrations in this solvent cannot be calculated accurately. For (I), the reciprocal relaxation time increases with increasing hydroxide ion concentration, but for (II) the relaxation time remains constant. Hence for (II) the first term of equation (2) makes the larger contribution whereas for (I) both terms contribute. This different behaviour is compatible with the different $pK_a^{0·1}$ values for (I) and (II). For (I), $k_r[H_2O]$ is taken as the value of the reciprocal relaxation time at the lowest hydroxide ion concentration. The rate coefficients k_f were calculated using the measured equilibrium constant in this solvent ($K = k_f/k_r$) and are shown in Table 3.

TABLE 3

Rate coefficients for proton transfer (1)

(a) 1,8-Bis(dimethylamino)naphthalene in aqueous solution

K	k_r/l mol^{-1} s^{-1}	k_f/l mol^{-1} s^{-1}
$2·9 \pm 0·7 \times 10^3$ (obs.)	70 ± 10 (obs.)	$1·9 \pm 0·4 \times 10^5$ (obs.)

(b) 1,8-Bis(dimethylamino)- (I) and 1,8-bis(diethylamino)-naphthalene (II) in 20% dioxan–water (v/v)

	$K[H_2O]^{-1}$/M^{-1}	$k_r[H_2O]$/s^{-1}	k_f/l mol^{-1}s^{-1}
(I)	630 ± 50 (obs.)	$7·3 \pm 0·6 \times 10^2$ (obs.)	$4·6 \pm 0·8 \times 10^5$ (calc.) *
(II)	40 ± 8 (obs.)	$1·14 \pm 0·08 \times 10^2$ (obs.)	$4·6 \pm 1·3 \times 10^3$ (calc.) *

* Calculated from the observed values of K and k_r.

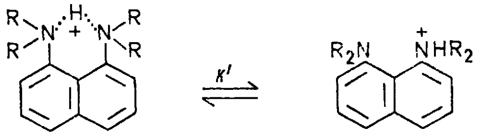
Proton Transfer for 1,8-*Diaminonaphthalene*.—Rate measurements of the equilibrium between 1,8-diaminonaphthalene (pK 4·61) [11] and its protonated form were made in aqueous solutions at pH *ca.* 4·5. In a solution containing equal concentrations of acetic acid and acetate ion (1×10^{-3}M), diaminonaphthalene (1×10^{-4}M), and potassium chloride (0·2M) a relaxation with τ *ca.* 3 μs was observed. This relaxation appeared as an increase in optical density at 335 nm and as a decrease at 285 nm which is compatible with the difference in extinction coefficients of (III) and its conjugate acid at these wavelengths. The relaxation time is within the heating time of the instrument and it is only possible to estimate a lower limit for the rate of proton transfer. Assuming our results refer to equilibrium (3) where B = (III), $k_f \sim k_r > 10^8$ l mol^{-1} s^{-1}.

$$BH^+ + CH_3CO_2^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B + CH_3CO_2H \qquad (3)$$

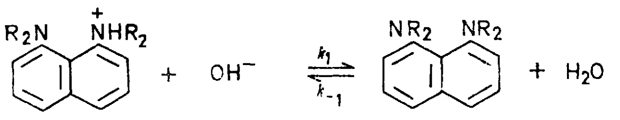
DISCUSSION

Proton transfers from (IH^+) and (IIH^+) to hydroxide ion are thermodynamically favourable yet occur at rates which are several orders of magnitude below those expected for the ionisation of a *normal* acid.[1] The rate coefficient for (IH^+) is $1·9 \times 10^5$ l mol^{-1} s^{-1} and for (IIH^+) the value is approximately two orders of magnitude lower still (Table 3). This behaviour contrasts with the *normal* ionisation behaviour of other substituted ammonium ions, for which diffusion controlled rates of *ca.* 3×10^{10} l mol^{-1} s^{-1} are observed.[1] Except for the reactions of proton cryptates,[12] the present rates are among the lowest measured for thermodynamically favourable proton transfer from nitrogen or oxygen acids to hydroxide ion.

The major factor responsible for the slowness is the presence of an intramolecular hydrogen bond in the protonated amines. One mechanism which can be written to explain the effect of the hydrogen bond[1] is shown in equations (4) and (5). An alternative mechanism involves direct attack by hydroxide ion on the proton in the hydrogen bond.[13] Assuming step (4) occurs rapidly and the equilibrium constant K' is $\ll 1$, the observed rate coefficients [equations (1) and (2)] are



(4)



(5)

$k_f = k_1K'/(1 + K') = k_1K'$ and $k_r = k_{-1}$. The overall equilibrium constant (K) for (1) is given by $K = K'K''$ and $K_a^{0\cdot1} = KK_w/[H_2O] = K'K''K_w/[H_2O]$ where K'' is the equilibrium constant for reaction (5). If the assumption is made that proton transfer to hydroxide ion from the intermediate without the internal hydrogen bond is diffusion controlled (k_1 3×10^{10} l mol^{-1} s^{-1}) approximate values of K' *ca.* 6×10^{-6} or ΔG° *ca.* 30 kJ mol^{-1} are obtained for the hydrogen bond in (IH^+). These results which correspond to a strong hydrogen bond can only be regarded as tentative since evidence will be presented below which indicates that k_1 may be slightly below the diffusion limit.

The present results can be compared with the rates of other slow proton transfers from intramolecularly hydrogen bonded acids.[1,14] Two examples involve proton transfer to hydroxide ion from a *trans*-bis(dimethylglyoximato)cobalt complex (k 6×10^4 l mol^{-1} s^{-1})[15] and from Clayton Yellow (k $2\cdot9 \times 10^4$ l mol^{-1} s^{-1}).[16] These together with the present systems are among the slowest such reactions involving nitrogen or oxygen acids which have been observed. This implies that in these cases, strong hydrogen bonds are involved. For (IH^+) other evidence supports this conclusion. The *X*-ray crystal structure[4] of (IH^+) shows a hydrogen bond having a short N · · · H · · · N distance as expected for a strong bond. The proton is thought to be almost symmetrically placed.[4,17] In addition, n.m.r. and i.r. spectra of solutions of (IH^+) are compatible with the presence of a strong hydrogen bond.[2] The factors which determine the strength of intramolecular hydrogen bonds are not well established but it appears that a six-membered ring (as here) is most favourable.[1b] Studies to investigate the strength of hydrogen bonds in other *peri*-substituted naphthalenes are in progress.

Solvent Isotope Effect.—The rate of proton removal by (I) from water is faster than that from deuterium oxide, $k_r(H_2O)/k_r(D_2O) = k_{-1}(H_2O)/k_{-1}(D_2O) = 2\cdot7 \pm 0\cdot5$. Similar isotope effects have been observed and discussed in detail for related systems.[14b] The observed effect is compatible with the mechanism shown in (4) and (5). The isotope effect $K''(H_2O)/K''(D_2O)$ can be estimated by assuming a value of $\Delta pK = 0\cdot5 \pm 0\cdot1$[18] for the difference in pK of the non hydrogen-bonded intermediate between H_2O and D_2O. Using the ratio of ionic products[19] for H_2O and D_2O, the result $K''(H_2O)/K''(D_2O) = 0\cdot4 \pm 0\cdot1$ is obtained. Therefore, since $K'' = k_1/k_{-1}$, the isotope effect on k_1 is small. This conclusion is compatible with a reactant-like transition state for proton transfer in (5) and with k_1 having a value close to the diffusion limit.

Comparison of Rates of Proton Transfer for 1,8-*Bis*(*dimethylamino*)- *and* 1,8-*Bis*(*diethylamino*)-*naphthalenes.*—Our analysis so far has assumed that the only factor responsible for the very slow rates is the presence of a hydrogen bond in (IH^+) and (IIH^+). We have assumed that k_1 in equation (5) is diffusion-limited and therefore that the observed rate coefficient (k_f) is determined by K' for the hydrogen bonding equilibrium (4). It will now be shown that the differences in rates for (I) and (II) (Table 3) cannot wholly be accounted for on the basis of different hydrogen bond strengths. In dioxan–water, the rate of proton transfer from (IH^+) to hydroxide ion is 10^2 times higher than the corresponding rate for (IIH^+). If k_1 is diffusion-limited for (I) and (II) this means that $K'(I)/K'(II) = 10^2$. This is compatible with the observed ratio of equilibrium constants $K(I)/K(II) = 16$ only if $K''(I)/K''(II) = 1/6$. The latter ratio is unlikely since the differences in pK of *NN*-dimethyl- and *NN*-diethyl-aniline and of trimethyl- and triethyl-amine[11] indicate that ethyl substitution should increase the pK_a and decrease K''. The value of K'' should also be smaller for (II) if the latter is more strained than (I). The relative rates and acidities are therefore not readily compatible with the same diffusion controlled value of k_1 for (I) and (II). The value of k_1 for (II) is probably lower than the value for (I) by a factor of between 6 and 100, corresponding to $K''(I)/K''(II)$ in the range 1—16. These two extremes represent the situations where the difference in pK between (I) and (II) is assumed to result

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[12] J. Cheney and J. M. Lehn, *J.C.S. Chem. Comm.*, 1972, 487.

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

[14] (*a*) E. M. Eyring and D. L. Cole, 'Nobel Symposium 5,' Interscience, New York, 1967, p. 255; (*b*) J. L. Haslam and E. M. Eyring, *J. Phys. Chem.*, 1967, **71**, 4470 and earlier papers.

[15] J. P. Birk, P. B. Chock, and J. Halpern, *J. Amer. Chem. Soc.*, 1968, **90**, 6959.

[16] M. Rose and J. Stuehr, *J. Amer. Chem. Soc.*, 1968, **90**, 7205.

[17] E. Haselbach, A. Henriksson, F. Jachimowicz, and J. Wirz, *Helv. Chim. Acta*, 1972, **55**, 1957.

[18] A. O. McDougall and F. A. Long, *J. Phys. Chem.*, 1962, **66**, 429.

[19] V. Gold, *Adv. Phys. Org. Chem.*, 1969, **7**, 259.

entirely from differences in K' and K'' respectively. The effect which brings about the lowering of k_1 and k_{-1} for (II) *could be a* transition state steric effect in reaction (5). This probably arises because in the transition state, the protonated dialkylamino-group must adopt a conformation which permits attack by hydroxide ion and in this conformation considerable strain is developed. The strain will be larger for (II) than for (I) but may contribute to the slowness of proton transfer for both (I) and (II). The difference in rates for (I) and (II) will be a result of this latter factor together with the difference in strengths of the intramolecular hydrogen bonds.

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