Protonation of Triaminobenzenes in Aqueous Solution: Reactions Involving Aromatic Compounds, σ-Complexes and Cyanine Ions

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The protonation of the 1,3,5-triaminobenzenes tripyrrolidinobenzene (TPB), methyltripyrrolidinobenzene (Me-TPB), ethyltripyrrolidinobenzene (Et-TPB), isopropyltripyrrolidinobenzene (Pr^i-TPB), trimorpholinobenzene (TMB) and tripiperidinobenzene (TPiB) has been studied. Data are reported for rate and equilibrium constants for the formation of σ-complexes (for TPB, TMB, TPiB, Me-TPB and Et-TPB), for equilibrium constants of the competing *N*-protonation (for TPB, TMB and TPiB) and for rate and equilibrium constants of the further *C*-protonation of σ-complexes leading to cyanine ions (for TPB, Me-TPB, Et-TPB and Pr^i-TPB).

Electrophilic aromatic substitutions, *i.e.* substitution of one electrophile (usually a proton) by another electron-deficient species, are the most important reactions of the aromatic ring. In these reactions a cyclohexadienyl cation is formed as intermediate, which is called a σ-complex. The present paper deals with the stability and reactivity of such σ-complexes, in order to understand better the influence of substituents, solvent and catalysts on the rate and product distribution of electrophilic aromatic substitution reactions.

The simplest example of these reactions is the replacement of one aromatic proton by another. For benzene the rate of this reaction has been measured in concentrated sulphuric acid by hydrogen isotope exchange, and the rate constant for the exchange[1] is 10^{-14} dm^3 mol^{-1} s^{-1}. Benzene acts as Lewis-base at the formation of the intermediate. However, benzene is an extremely weak base; its pK_a value[2a] has been estimated to be −23. The basicity of the aromatic ring may be increased by appropriate substituents; *e.g.* due to the introduction of a methoxy group, anisole[2a] has a pK_a value of −15.3. Addition of further methoxy or ethoxy groups leads to a further increase in the basicity, and for 1,3,5-triethoxybenzene[2a] we reach pK_a = −4.8. But even with this compound, concentrated acids have to be used as solvents for a study of the protonation, and therefore a quantitative interpretation of the results may be ambigious.

Azulenes are also aromatic according to the (4*n* + 2) Hückel rule. These molecules have strong dipole moments, where the five-membered ring carries the negative charge, and therefore it has a stronger tendency to bind protons. Correspondingly for appropriately substituted azulenes[3,4b] the basicity increases up to pK_a = 1.5. However, the results obtained with these non-benzenoid aromatic compounds may not be directly transferred to the reactivity of substituted benzenes.

Therefore we looked for benzenes with substituents of very high electron-donating character, in order to increase the basicity of the aromatic ring. We used cyclic amines as substituents, and studied the protonation of the following triaminobenzenes: 1,3,5-tripyrrolidinobenzene (TPB), 1,3,5-trimorpholinobenzene (TMB), 1,3,5-tripiperidinobenzene (TPiB) and 2-alkylated 1,3,5-tripyrrolidinobenzenes (X-TPB with X = Me, Et and Pr^i). Some results of these studies have already been presented.[5] This paper reports on further results, in which the range of the study has been extended and the accuracy of the measurements has been improved. Now the protonation reactions of these compounds are completely understood.

Of the substituents used, the pyrrolidino-group is the strongest electron donor due to the tendency to form exocyclic double bonds. Therefore a considerable rise in the pK_a is expected for tripyrrolidinobenzene, compared with the substituted benzenes investigated previously. We measured p$K_{a,1}$ = 9.62 spectrophotometrically for the first dissociation constant of $TPBH^+$. The proton may bind not only to an aromatic carbon but also to the nitrogen atom of a pyrrolidino ring. However, at pH ≃ p$K_{a,1}$ the spectrum changes drastically: the aromatic band disappears at the protonation and the three absorption bands of a σ-system appear, indicating that protons bind predominantly to the aromatic ring. This is confirmed by the kinetic study, since binding of a proton to a nitrogen atom proceeds with diffusion-controlled rate, whereas for the protonation of TPB a chemical relaxation is observed in the time range 10^{-3}–1 s. Over the range 8.7 < pH < 10.7 the reaction was studied using the pressure-jump relaxation technique.[5a] Relaxation times and relaxation amplitudes can be described quantitatively by the reaction shown in Scheme 1. (The indices 'C' and

$$TPB + H_2O \underset{k_{-1,OH}}{\overset{k_{1,OH}}{\rightleftharpoons}} TPBH_C^+ + OH^-$$

Scheme 1

'N' refer to the proton binding to a carbon atom and a nitrogen atom, respectively.) Both rate constants can be obtained experimentally, and the ratio of these constants yields a value for the dissociation constant which agrees with the spectrophotometrically determined value. This confirms Scheme 1, and reveals that the binding of protons to nitrogen atoms is negligibly small. This means that TPB forms σ-complexes $TPBH_C^+$, which are stable even in slightly alkaline solutions, where its stability and reactivity can easily be studied.

In Scheme 1 water acts as electrophile, whereas at pH < 8 protons bind directly to TPB.[5d] At pH < 1.5 a second protonation at another carbon atom of the aromatic ring is observed. Furthermore, if the reaction is performed at pH < 5, intermediates occur, where protons also bind to nitrogen atoms. This leads to the reaction in Scheme 2 for the protonation of TPB, see Fig. 1.

The spectra in Fig. 2 show the absorption bands of the aromatic compound TPB for pH > p$K_{a,1}$, the three absorption bands of the σ-complex $TPBH_C^+$ at lower pH, and a spectrum, which is due to the cyanine group, >N$^+$=CH–CH=CH–N<, of the ion $TPBH_CH_C^{2+}$, for pH < 0.5. The *N*-protonated ions $TPBH_N^+$ and $TPBH_NH_N^{2+}$ have not to be considered in the discussion of the spectra, since at equilibrium their concentrations are negligibly small, as will be shown later. According to Fig. 2, the formation of σ-complexes and cyanine ions can easily be detected in the UV–VIS region.

The equilibrium between the six different species is given by five dissociation constants as shown in eqns. (1)–(5), for the

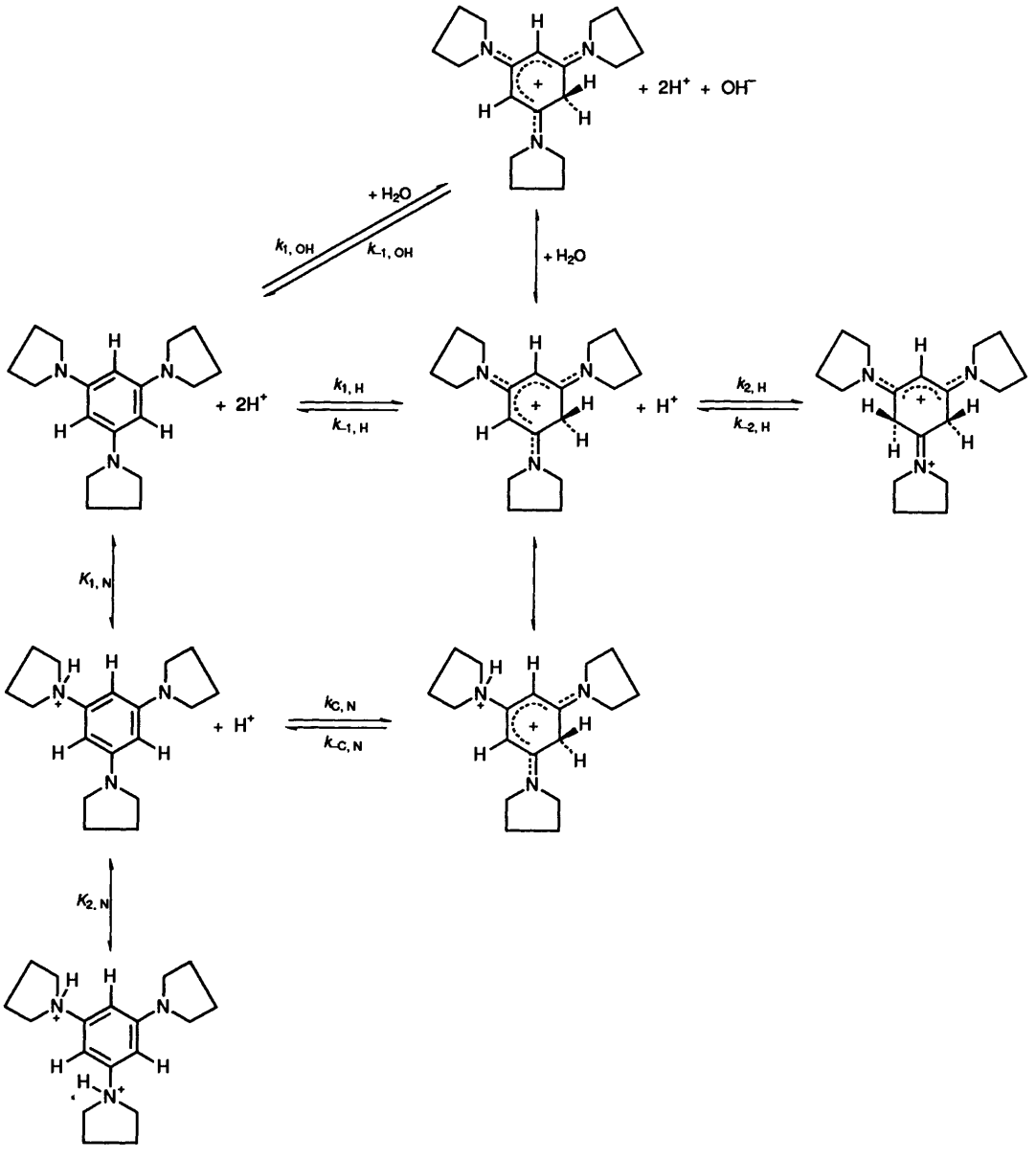

Fig. 1 Scheme 2 for the protonation of TPB. Double arrows (⇌) indicate rate determining steps; single arrows (⟷) indicate fast pre-equilibria

$$K_{1,C} = \frac{[H^+][TPB]}{[TPBH_C^+]} = \frac{k_{-1,H}}{k_{1,H}} \quad (1)$$

$$K_{2,C} = \frac{[H^+][TPBH_C^+]}{[TPBH_CH_C^{2+}]} \cdot \frac{f_I^2}{f_{II}} = \frac{k_{-2,H}}{k_{2,H}} \quad (2)$$

$$K_{1,N} = \frac{[H^+][TPB]}{[TPBH_N^+]} \quad (3)$$

$$K_{2,N} = \frac{[H^+][TPBH_N^+]}{[TPBH_NH_N^{2+}]} \cdot \frac{f_I^2}{f_{II}} \quad (4)$$

$$K_{2,CN} = \frac{[H^+][TPBH_N^+]}{[TPBH_CH_N^{2+}]} \cdot \frac{f_I^2}{f_{II}} \quad (5)$$

mono- and di-*C*-protonated, mono- and di-*N*-protonated, and mono-*C*-mono-*N*-protonated TPB, respectively. Parameters f_I and f_{II} are the activity coefficients of the mono- and divalent ions, respectively. They are estimated according to[6] eqn. (6).

$$-\log f_z = 0.5z^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.3I] \quad (6)$$

The first dissociation constant $K_{a,1}$ (mentioned above) is related to $K_{1,C}$ and $K_{1,N}$ by eqn. (7).

$$K_{a,1}^{-1} = \frac{[TPBH_C^+] + [TPBH_N^+]}{[TPB][H^+]} = K_{1,C}^{-1} + K_{1,N}^{-1} \quad (7)$$

Protons bind to nitrogen atoms with diffusion-controlled rate, whereas the binding to carbon atoms is relatively slow. Therefore, with the techniques used in this study, two relaxation effects can be observed, which correspond to the reaction of TPB with H^+ forming $TPBH_C^+$ and to the reaction of $TPBH_C^+$ with H^+ forming $TPBH_CH_C^{2+}$. The former reaction is studied over pH-ranges in which the concentration of $TPBH_CH_C^{2+}$ may be neglected. According to the reaction in Fig. 1 the rate law of this reaction is given by eqn. (8), where:

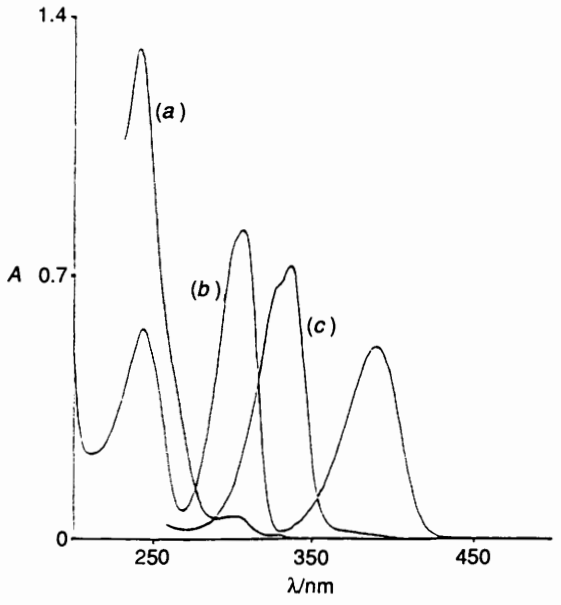

Fig. 2 Absorption spectra of solution of (*a*) TPB at pH = 12.5; (*b*) $TPBH_C^+$ at pH = 7.0; (*c*) $TPBH_CH_C^{2+}$ at pH = −0.5

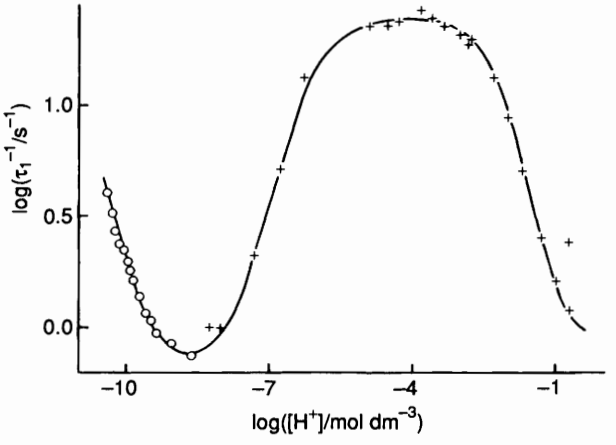

Fig. 3 Double logarithmic plot of the reciprocal relaxation time *versus* proton concentration for the first protonation of TPB; +: stopped flow data; ○: p-jump data; the curve is calculated according to eqn. (9) with the constants given in Table 1

$k_{-1,OH}/k_{1,OH} = K_{1,C}/K_W$; $k_{-1,H}/k_{1,H} = K_{1,C}$; and $k_{-C,N}/k_{C,N} = K_{2,CN}$. There is no indication of intramolecular proton transfer from nitrogen to carbon atoms. Therefore these reactions paths have not been considered in Fig. 1.

The σ-complex $TPBH_CH_N^{2+}$ is not detected in the spectra, and it is assumed, therefore, that its concentration is negligibly small. Furthermore, the solutions are buffered. Under these conditions we obtain for the relaxation time of the first protonation eqn. (9).

The second protonation (formation of $TBPH_CH_C^{2+}$) is much faster than the first. Thus the rate law for the second reaction, eqn. (10), leads to eqn. (11) for the relaxation time.

For stopped-flow experiments under first-order conditions, the relaxation time is equivalent to the observed rate constant k_{obs}. The results reported in this paper for the protonation of the different triaminobenzenes quantitatively agree with Scheme 2 with the equilibrium constants defined in eqns. (1)–(7) and the rate constants given in eqns. (8) and (10).

Experimental

The triaminobenzenes were kindly provided by Professor F. Effenberger from the University of Stuttgart.[7] Tridistilled water was used. All other chemicals were of analytical grade and bought commercially. In order to increase the solubility of the unprotonated triaminobenzenes, mixtures of water–ethanol, 90:10 v/v were used as solvents, if not indicated otherwise.

The kinetic measurements were performed with stopped-flow, pressure-jump and temperature-jump techniques.[8] The relaxation times were measured in the temperature range from 10–35 °C and were interpolated according to the Arrhenius' equation. Pressure-jump experiments were performed at final pressures of 1–1000 bar and were interpolated according to van't Hoff's equation. NMR spectra were obtained with a Bruker WP-80 and a Bruker Aspect-3000. UV–VIS spectra were measured with an Uvikon 860 instrument.

The pH was measured with a standard glass electrode. For pH < 4.3 and pH > 9.7 the proton concentration was adjusted by adding HCl and NaOH, respectively, and the solutions were carefully degassed in order to remove CO_2. For basic solutions the pH value was calculated with $pK_W = 14.2$ for the ion product of water in the solvent used.[9] In the intermediate pH-range, acetate and phosphate buffers were used. In all cases the pH-value measured agreed with those calculated from the concentrations of acids, bases and buffers within an error of ±0.03.

The results refer to 25 °C, 1 bar and water–ethanol, 90:10 v/v, if not indicated otherwise.

Results

Numerous measurements had to be performed in order to evaluate the equilibria and kinetics of the reactions involved in Fig. 1. Most of the experiments are described in detail in the thesis of W. S.,[10] and a listing of the individual results can be obtained from W. K. on request. In this chapter the experimental data are summarized.

Tripyrrolidinobenzene.—Due to experimental difficulties, the results reported previously[5d] were not accurate in the range pH < 6. We repeated those measurements, and for the whole pH range studied the experimental data are fitted to eqn. (9) as shown in Fig. 3. The agreement is excellent using the values $K_{1,C} = 2.4 \times 10^{-10}$ mol dm^{-3}, $K_{1,N} = 7.5 \times 10^{-7}$ mol dm^{-3},

$$-\mathrm{d}([TPB] + [TPBH_N^+] + [TPBH_NH_N^{2+}])/\mathrm{d}t = k_{1,OH}[TPB] + k_{1,H}[TPB][H^+] + k_{C,N}[TPBH_N^+][H^+]f_I^2f_{II}^{-1} - k_{-1,OH}[TPBH_C^+][OH^-]f_I^2 - k_{-1,H}[TPBH_C^+] - k_{-C,N}[TPBH_CH_N^{2+}] \quad (8)$$

$$1/\tau_1 = (k_{1,OH} + k_{1,H}[H^+] + k_{C,N}K_{1,N}^{-1}f_I^2f_{II}^{-1}[H^+]^2)\left\{\frac{1}{1 + K_{1,N}^{-1}[H^+] + K_{1,N}^{-1}K_{2,N}^{-1}f_I^2f_{II}^{-1}[H^+]^2} + \frac{K_{1,C}}{[H^+]}\right\} \quad (9)$$

$$\frac{\mathrm{d}[TPBH_CH_C^{2+}]}{\mathrm{d}t} = k_{2,H}[TPBH_C^+][H^+]f_I^2f_{II}^{-1} - k_{-2,H}[TPBH_CH_C^{2+}] \quad (10)$$

$$1/\tau_2 = k_{-2,H} + k_{2,H}f_I^2f_{II}^{-1}[H^+] \quad (11)$$

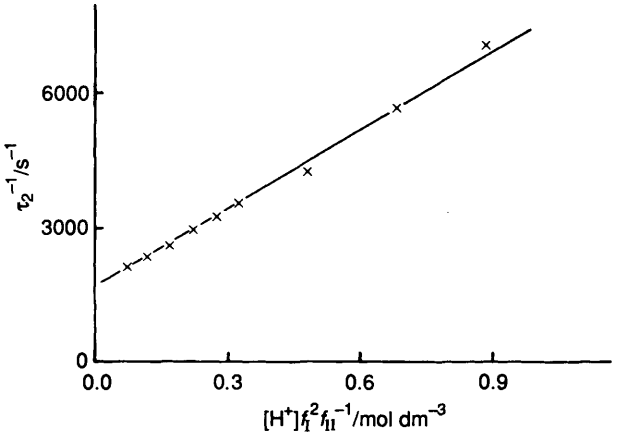

Fig. 4 Reciprocal relaxation time for the second protonation of TPB plotted according to eqn. (11)

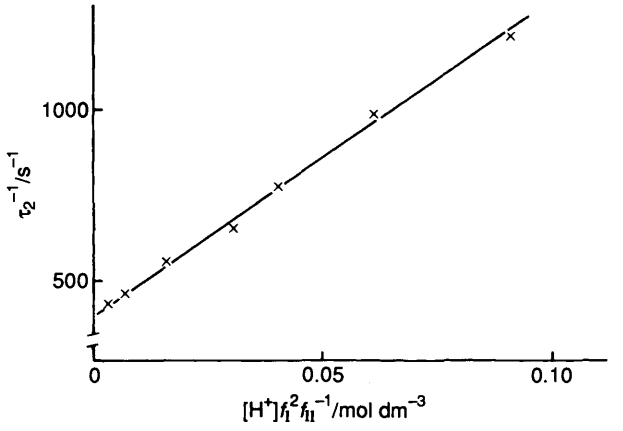

Fig. 5 Reciprocal relaxation time for the second protonation of Me-TPB *versus* proton concentration

$K_{2,N} = 7 \times 10^{-3}$ mol dm^{-3}, $k_{1,H} = 3.2 \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_{1,OH} = 0.62$ s^{-1} and $k_{CN} = 100$ dm^3 mol^{-1} s^{-1}.

As mentioned in the introduction, the protonation of TPB is studied using the pressure-jump technique in the range pH = pK_a ± 1, where the water molecule acts as electrophile and the reaction proceeds according to Scheme 1. Correspondingly, in this range eqn. (9) may be approximated by eqn. (9a). The

$$1/\tau = k_{1,OH}(1 + K_{1,C}[H^+]^{-1}) \quad (9a)$$

stopped-flow technique was applied in order to extend the studies to lower pH-values, where H_3O^+ is the electrophile. Below pH 8 the equilibrium is shifted nearly completely to $TPBH_C^+$, and the protonation may be considered as an irreversible process, *i.e.* the term $K_{1,C}[H^+]^{-1}$ may be neglected in eqn. (9). In the range 8 > pH > 6 the reaction rate is proportional to the proton concentration, and eqn. (9) is reduced to eqn. (9b). Between pH 5 and 3 the reaction rate is

$$1/\tau = k_{1,H}[H^+] \quad (9b)$$

nearly constant due to the competitive binding of protons to nitrogen atoms. This leads to eqn. (9c). Below pH 3, two protons

$$1/\tau = k_{1,H}K_{1,N} \quad (9c)$$

bind to two different nitrogen atoms of a TPB molecule. This leads to a linear decrease of the reaction rate with increasing proton concentration, and eqn. (9d) holds. Finally, below pH 1

$$1/\tau = k_{1,H}K_{1,N}K_{2,N}[H^+]^{-1}f_I^{-2}f_{II} \quad (9d)$$

a strong deviation from the linear decrease is observed. Here the isomerisation from $TPBH_N^+$ to $TPBH_C^+$ occurs partially *via* the diprotonated $TPBH_CH_N^{2+}$. This is taken into account by the rate constant k_{CN}, and eqn. (9e).

$$1/\tau = k_{1,H}K_{1,N}K_{2,N}[H^+]^{-1}f_I^{-2}f_{II} + k_{CN}K_{2,N} \quad (9e)$$

Between pH 8.7 and 4.3, the measurements had to be performed in buffered solutions. The reaction is generally acid-catalysed, and for these solutions the term $k_{HB}[HB]$ has to be added in eqn. (9). For acetic acid we obtain for the constant of catalysis $k_{HB} = (3 \pm 0.5) \times 10^5$ dm^3 mol^{-1} s^{-1}. Analogously we obtain $k_{HB} = (4 \pm 1) \times 10^3$ dm^3 mol^{-1} s^{-1} for $H_2PO_4^-$. The values for the relaxation times used in Fig. 3 are extrapolated to zero buffer concentration.

Below pH 1 the diprotonated $TPBH_CH_C^{2+}$ is observed. This species hydrolyses quickly, and the kinetics of the second protonation can be studied only by combining stopped-flow and temperature-jump techniques in the following way. The empty sample cell is assembled with the temperature-jump equipment and the capacitor is charged. In a stopped-flow apparatus a solution of $TPBH_C^+$ at pH *ca.* 5 is mixed with a solution of HCl in order to obtain the final pH. The mixed solution flows from the mixing chamber immediately into the temperature-jump cell, and the relaxation experiment is completed within less than 10 s after mixing the solutions. The results of these measurements are plotted in Fig. 4 according to eqn. (11).

From the straight line plot we obtain $k_{2,H} = (5800 \pm 350)$ dm^3 mol^{-1} s^{-1} and $k_{-2,H} = (1700 \pm 100)$ s^{-1}. The ratio of the rate constants yields $K_{2,C} = (0.29 \pm 0.03)$ mol dm^{-3}. In water–ethanol, 98:2 v/v, the value $K_{2,C} = 0.16$ mol dm^{-3} was calculated from the relaxation-amplitude of the hydrolysis reaction[5c] of TPB. The difference between these two values is due to the different composition of the solvents, as discussed later. Reaction enthalpies, reaction volumes and activation energies have been determined previously.[5a,d] All thermodynamic and kinetic data are summarized in Table 1.

2-*Methyl*-1,3,5-*tripyrrolidinobenzene* (Me-TPB).—For the first protonation our spectrophotometric and kinetic measurements yielded the same results as quoted in the previous study.[5d] The measurements were restricted to basic solutions, where the reaction proceeds according to Scheme 1. Rate constants were evaluated for the reaction of Me-TPB with water: $k_{1,OH} = (5.7 \pm 0.3) \times 10^{-3}$ s^{-1}; $k_{-1,OH} = (0.16 \pm 0.01)$ dm^3 mol^{-1} s^{-1}. Due to hydrolysis in acidic solutions, the direct protonation cannot be observed, and therefore for $k_{1,H}$ and $k_{-1,H}$ only an upper limit can be estimated from eqn. (9): $k_{1,H} \leqslant 1 \times 10^7$ dm^3 mol^{-1} s^{-1}; $k_{-1,H} \leqslant 2 \times 10^{-6}$ s^{-1}.

For Me-TPB the second protonation is studied which leads to a cyanine ion as indicated by its spectrum. This compound is more stable than $TPBH_CH_C^{2+}$, and the second dissociation constant $K_{2,C} = (4.3 + 0.5) \times 10^{-2}$ dm^{-3} mol^{-1} can be obtained by spectrophotometric titration. For the kinetic measurements the same technique is used as is described for TPB. In Fig. 5 the results are plotted according to eqn. (11). The slope and intercept of the straight line yield $k_{2,H} = (9000 \pm 400)$ dm^3 mol^{-1} s^{-1} and $k_{-2,H} = (400 \pm 20)$ s^{-1}, respectively. The dissociation constant is calculated from the ratio of the rate constants with the result $K_{2,C} = (4.4 \pm 0.4) \times 10^{-2}$ mol dm^{-3}, in agreement with the value mentioned above. Table 1 summarizes all constants including those obtained from temperature- and pressure-dependent measurements.

2-*Ethyl*-1,3,5-*tripyrrolidinobenzene* (Et-TPB).—The results[5d] reported for the protonation of Et-TPB are wrong. This is due to the fact that in the previous study the concentration of the compound was too high, and dissolution processes were super-

Table 1 Thermodynamic and kinetic parameters for the first and second protonation of tripyrrolidinobenzenes. (The values in brackets are estimated as described in the discussion.)

	TPB	Me-TPB	Et-TPB	Pr^i-TPB
$pK_{1,C}$	9.62	12.75	14.70	>15
$k_{1,H}$/dm^3 mol^{-1} s^{-1}	3.2×10^7	(3×10^5)	(7×10^6)	—
$k_{-1,H}$/s^{-1}	7.7×10^{-3}	(5×10^{-8})	(1.5×10^{-8})	—
$k_{1,OH}$/s^{-1}	0.62	5.7×10^{-3}	0.13	—
$k_{-1,OH}$/dm^3 mol^{-1} s^{-1}	2.4×10^4	0.16	4.1×10^{-2}	—
$\Delta H^{\ddagger}_{1,OH}/10^3$ J mol^{-1}	46	57	—	—
$\Delta S^{\ddagger}_{1,OH}$/J K^{-1} mol^{-1}	−90	−100	—	—
$pK_{2,C}$	0.53	1.37	1.55	2.21
$\Delta H^0_{2,C}/10^3$ J mol^{-1}	—	27	20	30
$\Delta S^0_{2,C}$/J K^{-1} mol^{-1}	—	60	30	60
$\Delta V^0_{2,C}$/cm^3 mol^{-1}	—	—	6	9
$k_{2,H}$/dm^3 mol^{-1} s^{-1}	5.8×10^3	9.0×10^3	5.4×10^3	7.5×10^3
$k_{-2,H}$/s^{-1}	1.7×10^3	400	160	46
$\Delta H^{\ddagger}_{2,H}/10^3$ J mol^{-1}	—	30	23	20
$\Delta S^{\ddagger}_{2,H}$/J K^{-1} mol^{-1}	—	−90	−110	−100

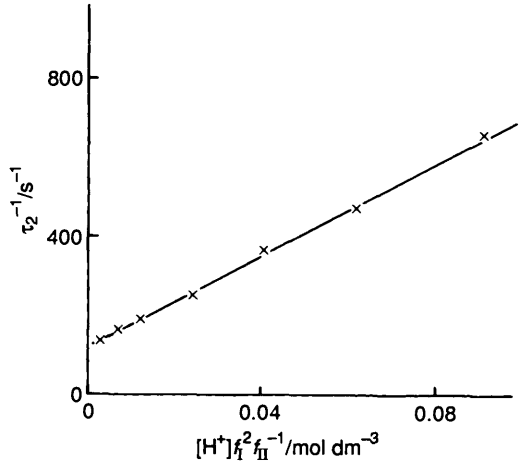

Fig. 6 Reciprocal relaxation time for the second protonation of Et-TPB *versus* proton concentration

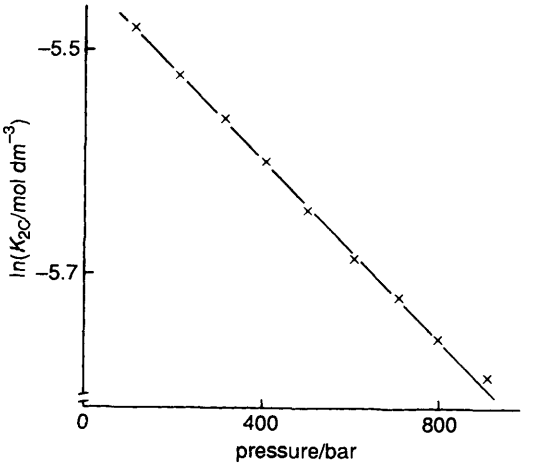

Fig. 7 Logarithmic plot of the equilibrium constant $K_{2,C}$ *versus* pressure for Pr^i–TPB

imposed on the protonation reactions. Therefore in the present investigation the concentration of Et-TPB is reduced to 6.5×10^{-6} mol dm^{-3}. The first dissociation constant $K_{1,C} = (2.0 \pm 0.3) \times 10^{-15}$ mol dm^{-3} is determined in 0.4–1.5 mol dm^{-3} NaOH. Kinetic measurements are performed in 0.05–0.5 mol dm^{-3} NaOH using the stopped-flow technique. For all solutions the same relaxation time of (7.6 ± 0.3) s is observed. This independence on the hydroxide-ion concentration agrees with eqn. (9a). Over the pH-range studied $K_{1,C}[H^+]^{-1}$ varies only between 0.07 and 0.01, and therefore the change expected for τ is within the range of experimental error. τ determines the value of $k_{1,OH}$ and together with $K_{1,C}$ also $k_{-1,OH}$: $k_{1,OH} = (0.13 \pm 0.02)$ s^{-1}; $k_{-1,OH} = (0.041 \pm 0.011)$ dm^3 mol^{-1} s^{-1}. Again for $k_{1,H}$ and $k_{-1,H}$ only an upper limit can be estimated: $k_{1,H} < 3.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1}; $k_{-1,H} \leqslant 7 \times 10^{-5}$ s^{-1}.

Below pH 3 diprotonated Et-TPB$H_CH_C^{2+}$ is formed, which decomposes slowly (half life of *ca.* 1 h). Thermodynamic and kinetic constants of the second protonation are obtained by photometric titration and temperature jump measurements, respectively, with the results $K_{2,C} = (2.8 \pm 0.2) \times 10^{-2}$ mol dm^{-3} and $k_{-2,H} = (160 \pm 10)$ s^{-1}; $k_{2,H} = (5400 \pm 300)$ dm^3 mol^{-1} s^{-1}. The value of $k_{-2,H}/k_{2,H} = 3.0 \times 10^{-2}$ mol dm^{-3} is in agreement with the spectrophotometrically-determined value of $K_{2,C}$. The data for the kinetic measurements are shown in Fig. 6. From temperature- and pressure-dependent measurements the parameters E_a, ΔH^0 and ΔV^0 are calculated; their values are given in Table 1.

2-Isopropyl-1,3,5-tripyrrolidinobenzene (Pr^i-TPB).—The spectrum of this compound shows the three absorption bands of a σ-complex in basic solutions up to 3 mol dm^{-3} KOH, and no aromatic band is observed. This means that $pK_{1,C} > 15$ for the σ-complex and that the first protonation of Pr^i-TPB cannot be investigated.

Pr^i-TPB is stable in acidic solutions. Therefore for this compound the thermodynamics and kinetics of the second protonation (*i.e.* the protonation of the σ-complex) are studied more extensively and the experiments are described here in more detail than for the other alkylated TPBs. Spectrophotometrically we obtain $K_{2,C} = (6.2 + 0.4) \times 10^{-3}$ mol dm^{-3}. When the pressure is increased to 900 bar, this value is reduced by (30 ± 6)%, corresponding to a reaction volume of $\Delta V^0_{2,C} = (9 + 2)$ cm^3 mol^{-1}. The logarithm of the equilibrium constant is plotted *versus* the pressure in Fig. 7. The reaction enthalpy $\Delta H^0_{2,C} = (-30 + 3)$ kJ mol^{-1} is determined from temperature-dependent measurements over the range 15–40 °C.

The kinetics of the second protonation are studied in the range pH = $pK \pm 1$ using the pressure-jump technique. The results shown in Fig. 8 lead to: $k_{2,H} = (7500 \pm 500)$ dm^3 mol^{-1} s^{-1}; $k_{-2,H} = (46 \pm 6)$ s^{-1}; $E_{a,2,H} = (23 \pm 2)$ kJ mol^{-1}; $E_{a,-2,H} = (54 \pm 2)$ kJ mol^{-1}. From these kinetic parameters we calculate $K_{2,C} = (6.1 \pm 1.2) \times 10^{-3}$ mol dm^{-3} and $\Delta H^0_{2,C} = (31 + 3)$ kJ mol^{-1}, in agreement with the spectrophotometric data. The kinetic measurements are performed at different final pressures. In Fig. 9 the logarithm of the reciprocal relaxation time is plotted *versus* the pressure. The activation volume is calculated by differentiating eqn. (11) with respect to pressure to give eqn. (12). According to these eqns. the values 10.3, 10.0 and 12.4 cm^3

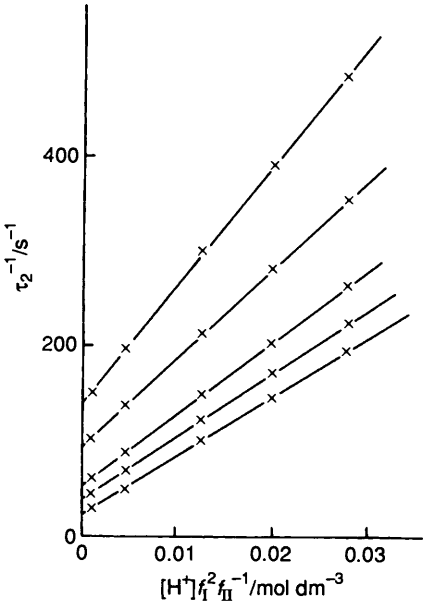

Fig. 8 Reciprocal relaxation time for the second protonation of Pr^i–TPB *versus* proton concentration at temperatures 17.2; 22.3; 26.7; 34.1; and 41.8 °C (from bottom to top)

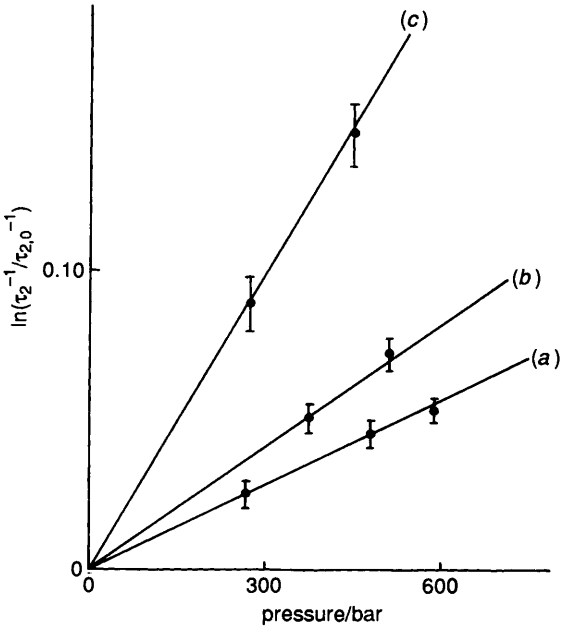

Fig. 9 Logarithmic plot of $\tau_2^{-1}/\tau_{2,0}^{-1}$ (index 0 refers to 1 bar) *versus* pressure for Pr^i-TPB at different concentrations of HCl: (*a*) 10^{-3} mol dm^{-3}; (*b*) 2×10^{-3} mol dm^{-3}; (*c*) 5×10^{-3} mol dm^{-3}

$$\left(\frac{\partial \ln \tau_2^{-1}}{\partial p}\right)_T = -\frac{\Delta V_{2,C}^{\ddagger}}{RT} - F\frac{\Delta V_{2,C}^{0}}{RT} \qquad (12)$$

$$F = \frac{K_{2,C}}{K_{2,C} + [H^+]f_I^2 f_{II}^{-1}}$$

mol^{-1} are obtained for $\Delta V_{2,C}^{\ddagger}$ from the straight lines in Fig. 9 at $[H^+] = 1.0 \times 10^{-3}$, 2.0×10^{-3} and 5.0×10^{-3} mol dm^{-3}, respectively; *i.e.* $\Delta V_{2,C}^{\ddagger} = (11 \pm 2)$ cm^3 mol^{-1}.

Dependence of Equilibrium and Rate Constants on Solvent Composition.—In order to determine the influence of the non-aqueous compound of the solvent on the mechanism of the reactions, we performed spectroscopic and kinetic measurements in binary aqueous solutions of different composition. The results of these studies are summarised in Table 2.

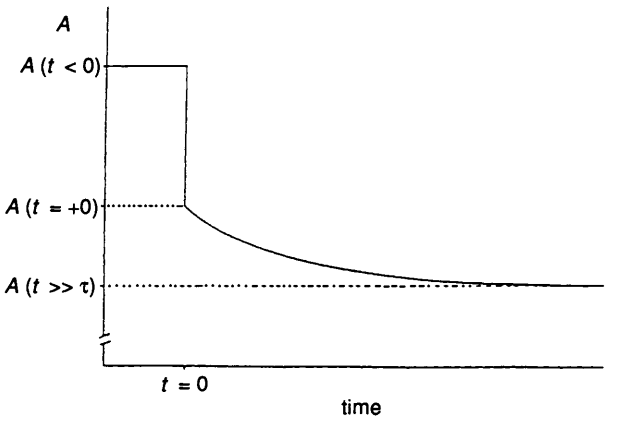

Fig. 10 Optical absorption *versus* time (schematically) indicating the formation of $TMBH_C^+$ in a stopped-flow experiment

Table 2 Equilibrium and rate constants for the second protonation of substituted tripyrrolidinobenzenes for different solvent composition

Compound	Solvent[a]	$pK_{2,C}$	$k_{2,H}$/dm^3 mol^{-1}s^{-1}	$k_{-2,H}$/s^{-1}
Pr^i-TPB	EtOH, 2%	2.61	12 700	31
	EtOH, 10%	2.21	7 500	46
	PrOH, 2%	2.60	12 000	30
	PrOH, 10%	2.36	8 000	35
Et-TPB	EtOH, 4%	1.85	8 050	115
	EtOH, 10%	1.53	5 400	160
Me-TPB	EtOH, 4%	1.67	14 000	300
	EtOH, 10%	1.35	9 000	400

[a] Aqueous solutions containing *x* vol% alcohol.

Position of C-*Protonation.*—For the substituted TPBs the σ-complexes are formed by the binding of a proton to the alkylated carbon atom of the aromatic ring (position 2). This is clearly indicated by the NMR spectra of deuteriated Me-TPBD$^+$, Et-TPBD$^+$ and Pr^i-TPBD$^+$ in D_2O. In all cases the two protons of the central ring (positions 4 and 6) give rise to a singlet at *ca.* 6 ppm. This means that these protons are magnetically equivalent and therefore the deuteron does not bind to positions 4 or 6.

1,3,5-*Trimorpholinobenzene* (TMB).—Protons bind predominantly to the nitrogen atoms of the morpholino rings and less to the aromatic carbon atoms. In the previous study,[5b] K_{CN} was calculated from the change in electric conductivity due

$$K_{CN} = \frac{[TMBH_C^+]}{[TMBH_N^+]} \qquad (13)$$

to the formation of $TMBH_C^+$. The present measurements are performed spectrophotometrically using methyl Orange (InH) as indicator. Methyl Orange is chosen since its protonation reaction is very fast, its pK is close to that of TMB, and the absorption bands of the two compounds are at different wavelength regions.

The formation of $TMBH_C^+$ is initiated in a stopped-flow experiment by jumping a solution containing TMB from pH $\gg$ $pK_{a,1}$ to pH $\approx$ $pK_{a,1}$, and it is observed at the wavelength of maximum absorption of the indicator (λ = 530 nm). The absorbance changes as shown in Fig. 10. The equilibrium between TMB and $TMBH_N^+$ is established in a first step, which

Table 3 Thermodynamic and kinetic parameters for the first protonation of unsubstituted triaminobenzenes

	TPB	TMB	TPiB
$pK_{1,C}$	9.62	2.45	4.64
$pK_{1,N}$	6.12	3.40	6.30
K_{CN}	1.6×10^3	0.11	0.022
$k_{1,H}$/dm^3 mol^{-1} s^{-1}	3.2×10^7	310	700
$pK_{2,N}$	2.15	1.07	3.49

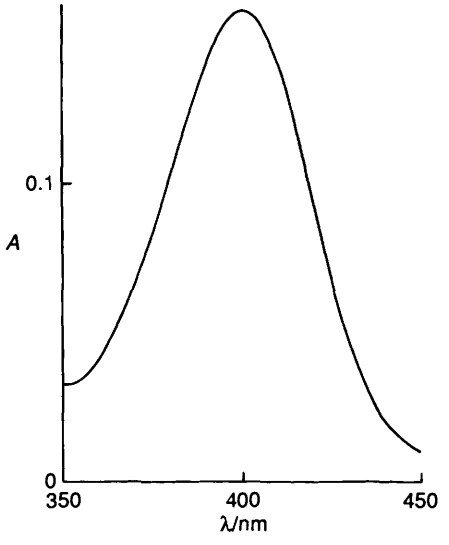

Fig. 11 Absorption spectrum of a solution of 3.76×10^{-4} mol dm^{-3} TPiB and 4×10^{-4} mol dm^{-3} HCl

is much too fast to be resolved by the technique applied, and therefore the relaxation time cannot be obtained for this step. In a second, much slower step $TMBH_C^+$ is formed, and a relaxation effect is observed. The amplitude of the effect, $A_1 = A(t = +0) - A(t \gg \tau)$, allows to calculate the change of concentration of methyl Orange, δ[InH], for this step. From δ[InH] the concentration changes of all species involved in the reaction are calculated by the following equations.

Due to the mass balance of the indicator we have eqn. (14).

$$\delta[InH] + \delta[In^-] = 0 \qquad (14)$$

Due to the mass balance of TMB we have eqn. (15).

$$\delta[TMB] + \delta[TMBH_C^+] + \delta[TMBH_N^+] = 0 \qquad (15)$$

Due to the mass balance of protons we have, in acidic solutions, eqn. (16).

$$\delta[TMBH_C^+] + \delta[TMBH_N^+] + \delta[InH] + \delta[H^+] = 0 \qquad (16)$$

Moreover TMB and $TMBH_N^+$ are in fast pre-equilibrium, which leads, for relatively small concentration changes, to eqn. (17).

$$\frac{\delta[TMB]}{[TMB]} + \frac{\delta[H^+]}{[H^+]} - \frac{\delta[TMBH_N^+]}{[TMBH_N^+]} = 0 \qquad (17)$$

Correspondingly we have, for the fast pre-equilibrium between InH and In^-, eqn. (18).

$$\frac{\delta[In^-]}{[In^-]} + \frac{\delta[H^+]}{[H^+]} - \frac{\delta[InH]}{[InH]} = 0 \qquad (18)$$

The five eqns. (14)–(18) contain six changes of concentration δ[X]. Since one of those, δ[InH], is obtained from the experiment, the others can be calculated.

Table 4 Absorption coefficients and wavelengths of maximum absorption for σ-complexes of triaminobenzenes

Species	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
Pr^i-$TPBH_C^+$	406	14 800
Et-$TPBH_C^+$	400	16 600
Me-$TPBH_C^+$	398	17 900
$TPBH_C^+$	387	20 800
$TMBH_C^+$	400	20 600

In the stopped-flow experiment the concentration jump is performed from pH ≫ $pK_{a,1}$, *i.e.* from a range, where TMB is quantitatively unprotonated. Therefore at the beginning of the slow relaxation, there is no $TMBH_C^+$ present in the solution, and the change in concentration is equal to the final concentration of $TMBH_C^+$, *i.e.* $\delta[TMBH_C^+] = [TMBH_C^+]$. This value, and the spectrophotometrically determined dissociation constant $K_{a,1} = 10^{-3.45}$ mol dm^{-3} (eqn. 7), allow K_{CN} to be calculated.

K_{CN} changes from 0.082 at 15 °C to 0.117 at 30 °C corresponding to a reaction enthalpy of $\Delta H_{CN} = (17 \pm 4)$ kJ mol^{-1}. This result agrees with the statement in the literature[11] that for triaminobenzenes the ratio K_{CN} increases with increasing temperature. The constants are summarized in Table 3.

1,3,5-*Tripiperidinobenzene* (TPiB).—In the previous study for this compound protonation to nitrogen atoms only was observed, with the dissociation constants $K_{1,N} = (5.0 \pm 0.4) \times 10^{-7}$ mol dm^{-3} and $K_{2,N} = (3.2 \pm 0.2) \times 10^{-4}$ mol dm^{-3}. However, by examining the UV–VIS spectrum of a solution of $TPiBH^+$ at unusually high concentration (see Fig. 11), a weak absorption at λ = 400 nm is detected, which must be due to a σ-complex according to the spectra in Fig. 1. The equilibrium between this σ-complex and $TPiBH_N^+$ cannot be determined by titration, since these ions are isomeric compounds. Furthermore the absorption is too weak for a determination of the equilibrium by evaluating relaxation amplitudes, as performed for TMB.[5b] We therefore calculate this constant from the value of the absorption with an estimated absorption coefficient. For that purpose we compare the coefficients at maximum absorption ε_{max} for the different σ-complexes in Table 4. They decrease with increasing size of the alkyl substituents, but for $TPBH_C^+$ and $TMBH_C^+$ they are nearly equal. Therefore we assume that ε_{max} of $TPiBH_C^+$ does not differ much from the corresponding value of $TPBH_C^+$.

Thus we can obtain $[TPiBH_C^+]$ from the spectrum in Fig. 11. Since under the experimental conditions TPiB exists completely in its monoprotonated form, this value allows us to calculate $K_{CN} = 0.022 \pm 0.004$ and $K_{1,C} = (2.3 \pm 0.5) \times 10^{-5}$ mol dm^{-3}. This means that 98% of the protons bind to nitrogen atoms and only 2% to aromatic carbon atoms.

The kinetics of the formation of the σ-complex are studied using the stopped-flow technique by moving from pH > $pK_{1,N}$ to pH < $pK_{1,C}$. For $K_{1,C} \gg K_{1,N}$ eqn. (9) may be reduced to eqn. (19). Since the second term on the right hand side of eqn.

$$1/\tau_1 = k_{1,H}K_{1,C} + k_{CN}K_{CN}^{-1}[H^+]f_{11}^{2-1} \qquad (19)$$

(19) is strongly dominant at most proton concentrations, Fig. 12 shows the results in a double-logarithmic plot. For high proton concentrations we obtain a straight line with slope 1 and $k_{CN}K_{CN}^{-1} = 22$ s^{-1}. The deviation from this line at low proton concentrations yields $k_{1,H}K_{1,C} = (1.6 \pm 0.8) \times 10^{-2}$ s^{-1}. Together with the equilibrium constants these data lead to $k_{1,H} = 700$ dm^3 mol^{-1} s^{-1} and $k_{CN} = 0.5$ s^{-1}. Table 3 summarizes the results together with the data for TPB and TMB.

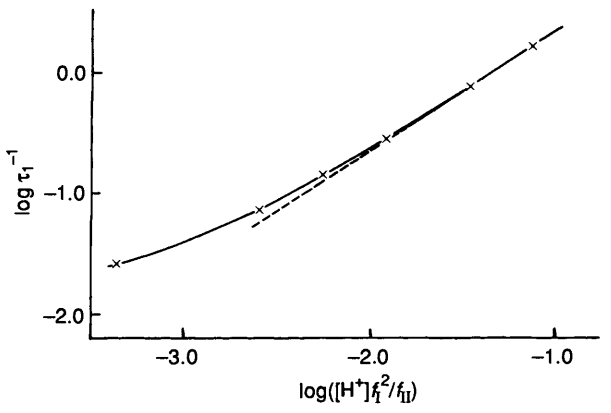

Fig. 12 Double logarithmic plot of $1/\tau_1$ *versus* $[H^+]f_I^2f_{II}^{-1}$ for the first protonation of TPiB. The curve is calculated according to eqn. (19) with the constants given in the text.

Discussion

The results presented in this paper prove the basic properties of the aromatic ring system of triaminobenzenes (TABs). The binding of a proton leads to the suspension of the aromatic system as indicated by UV–VIS data, kinetic measurements, and ^{1}H NMR studies. In the UV–VIS spectrum the protonation causes the disappearance of the aromatic absorption band and the simultaneous appearance of the three bands of the σ-complex, see Fig. 2. The rate of protonation is relatively small, indicating that the proton binds to a carbon and not to a nitrogen atom of the amino groups, where the reaction would be diffusion controlled and therefore very fast. In the NMR spectra the signal of the aromatic protons is diamagnetically shifted by *ca.* 1 ppm when a deuteron is bound. This is due to the loss of the aromatic structure. Furthermore, the NMR data reveal the position of the protonation for 2-alkyl substituted tripyrrolidinobenzenes. When a deuteron is bound, only one resonance signal for the two hydrogen atoms of the central ring is observed. This means that the two hydrogens are magnetically equivalent and therefore the deuteron (or the proton) binds to the alkyl-substituted carbon atom.

The σ-complexes are tris(dialkylamino)cyclohexadienyl ions, which are stabilized by the strong mesomeric properties of the nitrogen atoms in the *ortho* and *para* positions. The TABs are therefore basic and protonation of the aromatic ring occurs already in weakly acidic or even alkaline solution. The five-membered ring of the pyrrolidino group has a stronger tendency to form exocyclic double bonds than the six-membered rings of the morpholino and piperidino substituents.[12] Correspondingly TPB is more basic than TMB and TPiB. On the other hand, the strong influence of alkyl substituents in the 2 position on $pK_{1,C}$ cannot be explained by the weak inductive effect of the alkyl group, but has to be due to steric effects.[13] For X-TPB the alkyl group points out of the plane of the benzene ring leading to a disturbance of the aromatic system. This effect is stronger for more bulky substituents and therefore $pK_{1,C}$ increases from Me-TPB to Et-TPB and Pr^i-TPB, see Table 1. In the protonated X-TPBH$^+$ the alkyl substituent is in a quasi-axial position.

The spectra of TMBH$^+$ and TPiBH$^+$ show that at equilibrium protons bind to N- as well as to C-atoms, whereas the *N*-protonated TPBH$_N^+$ is only observed as an intermediate in the kinetic studies. The $pK_{1,N}$ values (see Table 3) correlate well with the pK_a values of the amines: pK_a = 11.27 for pyrrolidine, pK_a = 11.12 for piperidine and pK_a = 8.33 for morpholine. This correlation is less pronounced for the second *N*-protonation.

The discussion of the rate constants is limited by the fact that for TMB and TPiB only $k_{1,H}$ and for the alkylated TPBs only $k_{1,OH}$ can be measured. However, for the latter ones $k_{1,H}$ may be estimated from the rate constants obtained for TPB (including the constants of catalysis) in the following way: according to the Brönsted relation, for proton-transfer reactions the logarithm of the rate constant decreases approximately linearly with the pK_a of the proton donor. Therefore, we write our reaction as Scheme 3, and correlate the data: log k_1 (= log $k_{1,H}$) = 7.5 and pK_a =

$$TPB + HB \xrightarrow{k_1} TPBH^+ + B^-$$

Scheme 3

−1.7 for H_3O^+; log k_1 (= log k_{HB}) = 5.5 and pK_a = 4.75 for acetic acid; log k_1 (= log k_{HB}) = 3.6 and pK_a = 7.2 for $H_2PO_4^-$ and log k_1 (= log $k_{1,OH}$) = −1.9 and pK_a = 15.7 for H_2O. (For the pK_a values of H_3O^+ and H_2O, see Bell.[14]) The Brönsted relation is observed, and we assume that the difference between log $k_{1,H}$ and log $k_{1,OH}$ is approximately the same for the substituted X-TPBs as for the unsubstituted TPB (corresponding to the same slope of the Brönsted plot for all TPBs). This allows us to estimate $k_{1,H}$ for Me-TPB and Et-TPB. The estimated values are in agreement with the experimentally obtained upper limits for these constants, and they are included in Table 1.

The protonation of aromatic rings has been studied by Kresge *et al.* for alkoxybenzenes,[2] by Long *et al.* for azulenes,[4] by Alexander *et al.*[15] and by Terrier *et al.*[16] for pyrroles. Most of the kinetic data for those systems have been obtained by isotope exchange measurements, *i.e.* protodetritiation of tritium-

$$ArT + H^+ \underset{k_{-1,H}}{\overset{k_{1,H}}{\rightleftharpoons}} ArTH^+ \xrightarrow{k_{-1,T}} ArH + T^+$$

Scheme 4

labelled compounds. By this method the rate constant of exchange, k_{exch}, is measured, which is related to $k_{1,H}$ by the reaction mechanism given in Scheme 4, leading to eqn. (20).

$$k_{exch} = k_{1,H}\left(1 + \frac{k_{-1,H}}{k_{-1,T}}\right)^{-1} \quad (20)$$

The application of eqn. (20) has been discussed extensively by Terrier,[16] who proposes $k_{-1,H}/k_{-1,T}$ = 18. In order to be able to compare the rate constants, the statistical factor q has to be considered, which accounts for the number of equivalent basic sites of the aromatic compound. In this way the rate constants are obtained, eqn. (21), which are summarized in Table 5 together with the pK_a values.

$$k = k_{1,H}/q \quad (21)$$

Fig. 13 shows the Brönsted plot of the results. (The values for benzene and anisole are omitted, since they are obtained by very large extrapolations.) Most of the data fit well to a straight line with slope α = 0.56. The deviations for the trimethylpyrroles have already been discussed.[16] The results for tripiperidinobenzene are loaded with a relatively large error, since for this compound protons bind predominantly to nitrogen atoms and therefore the concentration of the σ-complex is very small. This error may—at least in part—cause the deviation of this point from the straight line. The reaction rate of the alkylated TPBs is strongly influenced by steric effects,[5d,13] which are not reflected by a Brönsted relation. Therefore, for these compounds the points deviate strongly from the average straight line.

The strong electron-donating power of the pyrrolidino group is also evident from the fact that in acidic solutions the σ-complexes can be further protonated to X-TPBH$_C$H$_C^{2+}$. The

Table 5 Rate and equilibrium constants for σ-complex formation; k_{exch}, rate constant of protodetritiation; $k_{1,H}$, rate constant of protonation; k, statistically corrected rate constant of protonation [see eqns. (20) and (21)]; all rate constants in $dm^3\ mol^{-1}\ s^{-1}$

Compound	pK_a	k_{exch}	$k_{1,H}$	q	log k	Ref.
Benzene	−23	6.3×10^{-16}	—	6	−15	1,2
Anisole	−15.3	1.6×10^{-9}	—	3	−8.0	2
1,3-Dimethoxy-2-methylbenzene	−9.3	8.5×10^{-6}	—	2	−4.09	2
1,3-Dimethoxybenzene	−9.0	7.9×10^{-6}	—	2	−4.12	2
1,3-Dihydroxy-2-methylbenzene	−7.5	3.6×10^{-4}	—	2	−2.43	2
1,3,5-Trimethoxybenzene	−5.7	6.2×10^{-3}	—	3	−1.41	2
1,3,5-Triethoxybenzene	−4.8	1.3×10^{-3}	—	3	−1.10	2
Azulene	−1.7	0.18	—	2	0.24	3,4
Guaiazulene-2-sulphonate	−0.6	0.85	—	2	0.91	4(*b*)
1,2,5-Trimethylpyrrole	0.0	200	—	2	3.28	15
4,6,8-Trimethylazulene	0.5	4.0	—	2	1.58	4(*b*)
1,3,4-Trimethylpyrrole	1.40	190	—	2	3.26	15
Guaiazulene	1.42	—	92	1	1.96	4(*b*)
TMB	2.45	—	310	3	2.01	—
2,4-Dimethyl-3-ethylpyrrole	3.75	—	5.7×10^3	1	3.76	16
TPiB	4.64	—	700	3	2.37	—
TPB	9.67	—	3.2×10^7	3	7.02	—
Me-TPB	12.75	—	3×10^5	1	5.50	—
Et-TPB	14.7	—	7×10^6	1	6.85	—

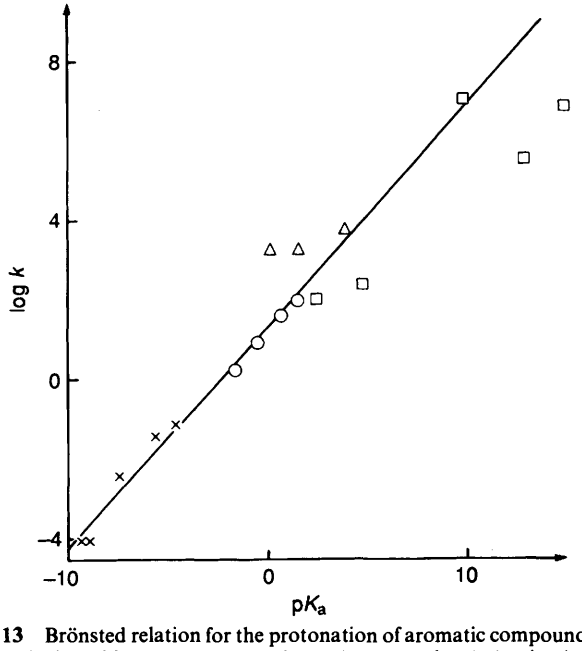

Fig. 13 Brönsted relation for the protonation of aromatic compounds; (×), substituted benzenes; (○), azulenes; (△), pyrroles; (□), triaminobenzenes

stability of the diprotonated benzenes depends weakly on the alkyl substituent, as seen in Table 1. The small changes in rate and equilibrium constants are due to the different size of the substituents leading to different steric interactions between the alkyl and the amino groups. Since the second protonation does not occur at the alkyl-substituted carbon atom, these interactions are much weaker than for the first protonation.

The influence of the solvent composition on the reaction rate (see Table 2) can be explained by the different solvation of the proton and the X-TPBH$^+$ ion. The carbon atoms of the central ring of the σ-complex are hydrophobic and with increasing alcohol concentration they are more strongly solvated by alcohol molecules. On the other hand, the proton is selectively solvated by water. Therefore, an increase in the alcohol concentration leads to a larger difference in the composition of the solvation shells of the reaction partners and therefore to a decrease of the forward reaction constant $k_{1,H}$. In the protonated X-TPBH$_C$H$_C^{2+}$ ion atoms carrying charges are selectively solvated by water, whereas the hydrophobic rings are selectively solvated by alcohol molecules. This disturbed solvation shell increases the backward rate constant $k_{-1,H}$. The influence of the solvent composition on the rate of σ-complex formation has been discussed previously.[5a]

To summarize, it may be said that the rate and equilibrium of the σ-complex formation of TABs correlate well with data for the protonation of other aromatic systems. That is, the mechanism of electrophilic aromatic substitution reactions is independent of the electron density of the aromatic ring (which is varied over a wide range by the appropriate choice of substituents) and strong deviations from the Brönsted plot in Fig. 13 can be explained by steric effects. Furthermore, for the first time it can be shown that the σ-complex can be protonated at a second carbon atom of the central ring. This leads to a dication containing the cyanine group >N–C=C–C=N$^+$<.

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