Basicity of some P_1 phosphazenes in water and in aqueous surfactant solution†

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Received 23rd February 2006, Accepted 20th March 2006
First published as an Advance Article on the web 18th April 2006
DOI: 10.1039/b602797k

The pK_a values in water and in dilute surfactant solution for 15 ring-substituted phenyl P_1 pyrrolidino phosphazenes PhN=P(NC_4H_8)$_3$ and the phenyl P_1 dimethylamino phosphazene PhN=P(NMe_2)$_3$ previously studied in acetonitrile (AN) and tetrahydrofuran (THF) are reported. The nonionic surfactant Tween 20 was used for the basicity measurements of some compounds to overcome the solubility problems. Measurements with a control group of phosphazenes in both media were used to validate the use of the obtained pK_a values as estimates of aqueous values. The pK_a values of the studied phosphazenes in aqueous medium vary from 6.82 (2,6-dinitro-) to 12.00 (4-dimethylamino-). The basicity span is 5.18 pK_a units. The aqueous pK_a values of the P_1 phosphazenes were correlated with the respective basicity data in AN and THF and from these correlations the pK_a values in water for the parent compounds HN=P(NC_4H_8)$_3$ and HN=P(NMe_2)$_3$ were estimated as 13.9 and 13.3. Also a comparison of the basicity of phosphazenes and some guanidines, amines and pyridines was made. In water the parent phosphazenes and guanidines are the strongest of all the groups of bases studied. In AN and THF the parent phosphazenes are clearly the strongest bases followed by guanidines, amines and pyridines which are bracketed between the basicities of phenyl phosphazenes. In the gas phase the phosphazenes for which data are available are clearly more basic than the other compounds referred to here. Comparison of the basicity data of P_1 phosphazenes and some guanidines confirms earlier conclusions about the partly ylidic character of the N=P double bond.

1 Introduction

In the course of our research aimed at design and basicity measurements of strongly basic phosphazene bases their basicity has been earlier investigated in acetonitrile[1–2] (AN), in tetrahydrofuran[3–5] (THF) and in the gas phase.[4] However, to the best of our current knowledge, no basicity data of phosphazenes in the most common solvent-water-are available. This is probably due to the low solubility of most of the alkylated phosphazene bases used in practice and also due to the high basicity of many of them. Thus the aim of this work was to fill this gap by measuring the pK_a values of a series P_1 phosphazenes in water (see Scheme 1 for compound definitions, numbering and acronyms) and to compare the basicities of phosphazenes in water and in other media.

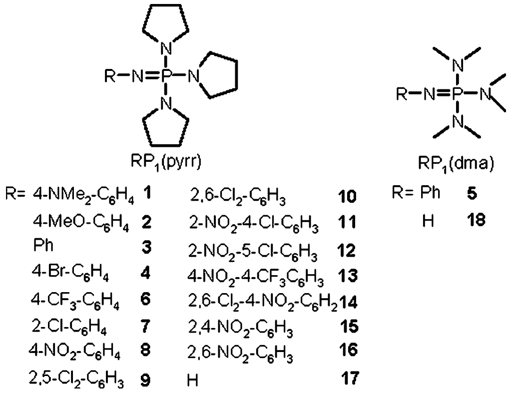
The basicity of a neutral base B in solvent S is commonly expressed as the dissociation constant K_a of the conjugate acid BH^+ of the base or as its negative logarithm pK_a:

$$BH^+ + S \rightleftarrows B + SH^+ \quad (1)$$

$$K_a = \frac{a(SH^+)a(B)}{a(BH^+)},\ pK_a = -\log K_a \quad (2)$$

where *a* is the activity of the corresponding species.

The solubility in water of all the phosphazene bases studied in this work is limited. With some bases it was possible to make aqueous solutions of sufficient concentration. With others the measurements were conducted in dilute solutions of nonionic surfactant Tween 20 to improve the solubility.



Scheme 1 Structures of the phosphazene bases measured in this work.

A number of studies of acidic and basic properties of molecules in surfactant solutions have been carried out.[6–10] A study of spectral and acid–base properties was carried out with some solvatochromic acid–base indicators in self-assembled surfactant aggregates.[6] Another work carried out with acid–base indicators focused on tuning the pK_a values by changing the properties of the medium by adding different surfactants.[7] In ref. 8 the behavior of 2-aminofluorene was studied as a function of concentration of different surfactants of the Tween family at fixed pH value and as a function of pH at given Tween concentration. It was observed that the higher the concentration of Tween and also the larger the molecules of Tween used, the bigger were the shifts in the pK_a values obtained. It has also been reported that the

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† Electronic supplementary information (ESI) available: Colour version of Fig. 1 and example of the treatment of experimental data. See DOI: 10.1039/b602797k

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presence of surfactants leads to a change in the transition interval of acid–base indicators thymol blue and bromothymol blue.[9] The pK_a values of ascorbic and maleic acid were determined potentiometrically, spectrophotometrically and conductometrically in cationic, anionic and nonionic surfactants and it was concluded that the acid–base properties of these acids are dependent on the type and concentration of surfactants used.[10]

The data available from the literature thus suggest that surfactants often shift the pK_a values of acidic or basic species when compared to the pK_a values in pure water. In this work the shifts observed were very small as verified by the measurements with a control set of bases that had satisfactory solubility. This might be explained by the fact that the concentration of surfactant solution used in this work was 1–2 orders of magnitude lower than that used in other reports.[6–10]

2 Experimental

Chemicals

Synthesis, purification and identification of the used noncommercial phosphazene bases is described as follows: compounds **1–4**, **7**, **9–11**, **15** in ref. 11, compound **5** in ref. 12, compounds **6**, **12–14**, **16** in ref. 3 and compound **8** in ref. 2.

The surfactant Tween 20 was purchased from Fluka. The buffer solutions for spectrophotometric measurements were prepared from Tris (tris(hydroxymethyl)aminomethane) (Reakhim, grade "pure"), glycine (Reakhim, grade "pure for analysis"), potassium hydroxide (Reakhim, grade "chemically pure"). The 0.1 M hydrochloric acid was prepared from a concentrate in a sealed ampoule (Lach-Ner, "Normanal"). Potassium chloride was from Reakhim, grade "chemically pure".

Experimental setup

pK_a values of the bases were measured using a combined method of UV-Vis spectrophotometry and potentiometry. All spectrophotometric measurements were carried out using a Nicolet Evolution 300 spectrophotometer equipped with a Single Cell Peltier Device for thermostating the sample cell to 25.0 ± 0.1 °C. The spectrophotometer was controlled from a PC and the spectra were stored in a digital form for further data processing. Fused silica cells with an optical path length of 1 cm were used. pH measurements were carried out with Metrohm 713 pH Meter and WTW combined pH-electrode SenTix-42. The electrode was calibrated using four standard calibration solutions with the following pH values: 2.00, 4.00, 6.88 and 10.06. Also a buffer solution with a pH value of 12.00 was used when measuring the bases with higher pK_a values. A linear regression line was used for the calibration. The slope of the electrode system was in the range of 94.6 to 95.5% from the theoretical value of 59.16 mV per pH unit. The standard deviation of the calibration points from the calibration line was in the range of 0.03 to 0.06.

For the preparation of the solutions of a measured base a small amount of the latter was suspended in about 250 ml of distilled water or 0.1% (*i.e. ca.* 8×10^{-3} M) Tween 20 solution in water. The solution was stirred using a magnetic stirrer for several hours and in most cases left to stand overnight. Then the solution was filtered (approximately the first 100 ml of solution was discarded to avoid possible contamination from the filter) and the filtrate was used as the stock solution of the base. For the spectrophotometric measurement a series of working solutions were prepared by mixing 10 ml of the base stock solution with 2 ml of a buffer solution of approximately known pH value. The buffer solutions were prepared by mixing the following solutions: 0.1 M HCl, 0.2 M Tris (containing 0.1 M KCl), 0.2 M glycine (containing 0.1 M KCl) and 0.1 M KOH solution. The buffer solutions were prepared in such a way as to obtain working solutions with different indicator ratios for the base and with ionic strengths in the range of 0.015–0.025 M. One of the solutions was prepared with sufficiently acidic pH so that essentially the whole base would be in protonated form. If possible, *i.e.* if it did not lead to extremely high pH values or decomposition of the base, then one solution was prepared with sufficiently high pH to ensure that the base is in neutral form. This involved KOH solutions with ionic strengths up to the range 0.2–0.8 M. With each working solution the pH was measured and after that the spectrum of the solution was recorded. Distilled water (or the solution of Tween 20), to which the same buffer solution was added, was used as reference. The pK_a values were determined as mean values of 4 to 14 measurements with working solutions.

Compounds **1–6** and **8** were measured in both water and aqueous surfactant solution; for compounds **7** and **9–16** the dilute aqueous surfactant solution was the only suitable medium for measurements due to the limited solubility at higher pH values of the solution.

Calculation method

For the calculation of pK_a values from the absorbance data analytical wavelengths were picked for the compounds corresponding to the maximum difference in absorbances between the neutral and protonated form. Two calculation methods were used.

Method 1 uses the absorbances of both neutral and cationic forms of the base at the analytical wavelength. According to the Lambert–Beer Law the net absorbance at the analytical wavelength λ can be written as in eqn (3) (the optical path length, 1 cm, is equal for all measurements and is included in A^λ, and the absorbance caused by the solvent or solution where the base was dissolved is compensated for):

$$A_x^\lambda = [\mathrm{B}]\,\varepsilon_\mathrm{B}^\lambda + [\mathrm{BH}^+]\,\varepsilon_{\mathrm{HB}^+}^\lambda \qquad (3)$$

where ε_x^λ values are molar absorptivities of the respective species at wavelength λ.

Taking into account that $C_\mathrm{base} = [\mathrm{B}] + [\mathrm{BH}^+]$, $a(\mathrm{BH}^+) = [\mathrm{BH}^+]f$ and $a(\mathrm{B}) = [\mathrm{B}]$ in dilute aqueous solutions (in aqueous solution the activity coefficient of neutral form [B] is equal to unity) we obtain from eqn (2):

$$K_\mathrm{a} = \frac{a(\mathrm{H}^+)[\mathrm{B}]}{[\mathrm{BH}^+]f} \qquad (4)$$

From this it can be shown that

$$K_\mathrm{a} = \frac{a(\mathrm{H}^+)}{f}\,\frac{A_{\mathrm{BH}^+}^\lambda - A^\lambda}{A^\lambda - A_\mathrm{B}^\lambda} \qquad (5)$$

where $a(\mathrm{H}^+)$ is the activity of hydrogen ions, f is the activity coefficient of the base in the protonated form $[\mathrm{BH}^+]$, $A_{\mathrm{BH}^+}^\lambda$ is the absorbance of the solution of the base in protonated form, A_B^λ is the absorbance of the solution of the base in neutral form and A^λ is the absorbance of the solution containing both neutral and protonated forms. All absorbances are given at wavelength λ. In eqn (5) it is assumed that the overall concentration of the base C_{base} is the same in all solutions. The value of the activity coefficient f of $[\mathrm{BH}^+]$ was calculated using the Debye–Hückel equation.[13]

Method 2 was used for the stronger bases for which a solution containing only the neutral form of the base could not be prepared due to too high a basicity being necessary. Rearranging eqn (5) results in eqn (6):

$$A^{\lambda} = \frac{1}{K_{\mathrm{a}}} \frac{a(\mathrm{H}^+)}{f} (A^{\lambda}_{\mathrm{BH}^+} - A^{\lambda}) + A^{\lambda}_{\mathrm{B}} \qquad (6)$$

Eqn (6) represents a linear regression equation with slope $1/K_{\mathrm{a}}$ and with intercept A^{λ}_{B}. The calculation of the pK_{a} value for a base from the linear regression data is straightforward. For an example of the quantitative treatment of the experimental data, see Item 1 in the ESI.†

2.1 Results

The pK_{a} values of phosphazenes and some other bases are presented in Table 1.

Altogether 23 basicity measurements in water or 0.1% Tween 20 solution were carried out for 16 phosphazenes previously measured in acetonitrile and tetrahydrofuran.

3 Discussion

Validity of the aqueous pK_{a} values determined using the surfactant

Due to the limited solubility pK_{a} values of the compounds **7** and **9–16** presented in Table 1 have been determined in a 0.1% solution of nonionic surfactant Tween 20. Because of the hydrophobic interactions between the phosphazene molecules (and possibly also the phosphazenium cation) and the surfactant molecules the pK_{a} values obtained this way do not necessarily coincide with those obtained in pure water as solvent. Also, the pH electrode system (especially the reference electrode) may behave differently in 0.1% Tween solution from in the aqueous buffers where it was calibrated.

To assess the possible effect of the surfactant the pK_{a} values of those phosphazene bases that were sufficiently soluble in pure water (**1–6**, and **8**) were determined in both media. As can be seen from Table 1 the differences between the values are with both signs. The average difference is −0.022 pK_{a} units and the standard deviation of the differences is 0.055 pK_{a} units. This means that there is no well-defined systematic effect. The maximum difference was observed with **3** and was 0.08 pK_{a} units.

Similar measurements in both media were also made with some other bases: **20** and **23**. The agreement between the value obtained in water and the value obtained in 0.1% Tween 20 solution is good: the difference is 0.01 pK_{a} units for both **20** and **23**. These results validate our approach for pK_{a} determination of bases not readily soluble in water. Considering the very small average deviation given above it is clear that there is no need to introduce any correction factors and we can thus handle the obtained pK_{a} values as estimates of the aqueous pK_{a} values.

We estimate the combined uncertainty of the pK_{a} values determined directly in aqueous medium as ±0.15 pK_{a} units ($k = 2$). In the case of pK_{a} determination in Tween solution we estimate the effect of the surfactant on the pK_{a} values as ±0.1 pK_{a} units ($k = 2$). Combining these values according to the uncertainty propagation rules gives a combined uncertainty of ±0.18 pK_{a} units ($k = 2$) for the values determined in the surfactant solution. It is also

Table 1 The pK_{a} values of some phosphazenes in aqueous solution (this work, if not indicated otherwise), in acetonitrile (AN), in tetrahydrofuran (THF) and their gas-phase basicities (GB)

		pK_{a}				
Compound	Base	H_2O	0.1% Tween 20	AN[a]	THF[b]	GB/kcal mol^{-1}
1	4-NMe_2–$C_6H_4P_1$(pyrr)	12.00	12.07	23.88	17.1	
2	4-MeO–$C_6H_4P_1$(pyrr)	11.94	12.00	23.12	16.6	255.2[c]
3	PhP_1(pyrr)	11.52	11.60	22.34	15.9	252.0[c]
4	4-Br–$C_6H_4P_1$(pyrr)	11.23	11.27	21.19	15.3	
5	PhP_1(dma)	10.64	10.60	21.25	15.3	
6	4-CF_3–$C_6H_4P_1$(pyrr)	10.65	10.59	20.16	14.6	
7	2-Cl–$C_6H_4P_1$(pyrr)		9.98	20.17	13.2	251.1[c]
8	4-NO_2–$C_6H_4P_1$(pyrr)	9.22	9.24	18.51		
9	2,5-Cl_2–$C_6H_3P_1$(pyrr)		9.21	18.52	11.9	248.4[c]
10	2,6-Cl_2–$C_6H_3P_1$(pyrr)		9.00	18.56	11.8	
11	2-NO_2-4-Cl–$C_6H_3P_1$(pyrr)		8.37	17.68	10.8	
12	2-NO_2-5-Cl–$C_6H_3P_1$(pyrr)		8.33	17.27	10.1	
13	2-NO_2-4-CF_3–$C_6H_3P_1$(pyrr)		8.14	16.54	9.6	
14	2,6-Cl_2-4-NO_2–$C_6H_2P_1$(pyrr)		7.50	14.43	7.8	
15	2,4-NO_2–$C_6H_3P_1$(pyrr)		7.34	14.88	8.0	
16	2,6-NO_2–$C_6H_3P_1$(pyrr)		6.82	14.12	7.5	
17	HP_1(pyrr)	13.93[d]		27.01	20.8	255.1[e]
18	HP_1(dma)	13.32[d]		25.85	19.7	249.6[e]
	Reference compounds					
19	TMG	13.6[f]		23.3[g]	15.3	234.8[h]
20	PhTMG	11.77	11.76	20.84	14.0	240.4[i]
21	Pyrrolidine	11.27[f]		19.56	13.5	218.8[i]
22	Et_3N	10.7[j]		18.82	12.5	227.0[i]
23	4-NMe_2-Pyridine	9.66	9.65	17.95	11.2	232.1[i]

[a] Ref. 2. [b] Ref. 3 and 4. [c] Ref. 4. [d] Estimated from the pK_{a} values determined in AN and THF. [e] Ref. 18. [f] Ref. 19. [g] Ref. 20. [h] Ref. 16. [i] Ref. 21. [j] Ref. 22.

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necessary to mention that the uncertainties of the pK_a differences of the bases are smaller than this value due to the strong correlation of the values determined using the same method.

These experimental observations of the small influence of the surfactant on the pK_a values of bases are also supported by the general knowledge that the pK_a values of bases (that is pK_a values of their cationic conjugate acids) are far less sensitive to medium than the pK_a values of neutral acids. This is not unexpected since dissociation of a cationic acid involves only rearrangement of the cationic charge between different species in solution (eqn (1)) while dissociation of a neutral acid involves generation and separation of two charged species. As an example, comparison of pK_a values of a wide selection of different bases in water and DMSO from ref. 14 yields the following correlation: pK_a(H_2O) = − 0.317 + 1.023pK_a(DMSO); *s*(intercept) = 0.93, *s*(slope) = 0.11, $n = 31$, $r^2 = 0.764$, $S = 1.55$. One sees that not only the sensitivity but also the absolute pK_a values are similar in these rather different solvents. Another very relevant example is determination of pK_a values in solutions of quaternary ammonium salts.[15] It has been demonstrated that upon moving from water to a 7.75 molal solution of tetrabutylammonium bromide the pK_a value of various amines changes at most by only 1.21 pK_a units. At the same time 7.75 molal tetrabutylammonium bromide solution contains 71% of the salt, being thus a medium very different from water and far less water-like than the very dilute surfactant solution used in this work. Tetrabutylammonium bromide is itself a rather powerful surfactant providing thus a relevant comparison for this work.

pK_a values of phosphazenes in different media

As seen from Table 1 the pK_a values of substituted PhP$_1$(pyrr) phosphazenes vary from 6.82 (2,6-dinitro-) to 12.00 (4-(dimethyl)amino-). The whole span is thus 5.18 pK_a units. The comparison with AN and THF as well as with the gas phase shows, that as expected, the differentiating ability of water is the smallest among all the media considered. The same span in AN and in THF is nearly two times wider: 9.8 and 9.6 pK_a units, respectively. Another obvious trend is that as the polarity and solvating power of the medium decreases the relative basicity of phosphazenes with respect to other families of bases increases. Thus, while in water even amines can compete with most phenyl P$_1$ phosphazenes and tetramethylguanidine is stronger than any of the studied phenyl P$_1$ phosphazenes, in the gas phase the same phosphazenes are distinctly the strongest bases among those studied.

Correlation of the phosphazene pK_a values (compounds **1–16**) in water and AN results in the following equation: pK_a(H_2O) = − 0.920 + 0.550pK_a(AN); *s*(intercept) = 0.48, *s*(slope) = 0.025, $n = 16$, $r^2 = 0.972$, $S = 0.29$. Correlation of the phosphazene pK_a values in water and THF yields the correlation line pK_a(H_2O) = 3.06 + 0.522pK_α(THF); *s*(intercept) = 0.22, *s*(slope) = 0.017, $n = 16$, $r^2 = 0.986$, $S = 0.22$. The available amount of gas-phase data is too small to obtain a meaningful correlation between the aqueous pK_a values and the gas-phase acidities. In order to compare the basicity of different types of P$_1$(pyrr) and P$_1$(dma) phosphazenes, it would be interesting to know also the aqueous pK_a values of the parent compounds HP$_1$(pyrr) and HP$_1$(dma). As these compounds are obviously too basic for direct measurement in aqueous solution and do not have chromophores for the spectrophotometric method, we took advantage of the correlations given above. Using these correlations of the phosphazene pK_a values in water and AN or THF, it is possible to predict the pK_a values of HP$_1$(pyrr) and HP$_1$(dma) in aqueous solution. Both correlations, *i.e.* correlation with AN and THF resulted in very similar pK_a values for both HP$_1$(pyrr) and HP$_1$(dma). For HP$_1$(pyrr), these pK_a values are 13.95 (correlation with AN) and 13.91 (correlation with THF), for HP$_1$(dma) these values were 13.31 and 13.33, respectively. Thus the estimates of the pK_a values of HP$_1$(pyrr) and HP$_1$(dma) can be obtained as follows: 13.9 and 13.3. These estimates are somewhat crude but allow us to draw qualitative conclusions.

It is of interest to compare the pK_a values of the pyrrolidinyl- and dimethylaminophosphazenes **3** and **5**. The pyrrolidinyl phosphazene is stronger in all media, the differences being 0.88, 1.09 and 0.60 pK_a units in water, AN and THF respectively. Using the correlations above, the basicity differences can be normalized to a common medium (water in this case) by multiplying them with the slopes of the respective correlation lines. The following basicity differences are then found for water, AN and THF: 0.9, 0.6, and 0.3 respectively. The different differentiating ability of the solvents is taken into account by the normalization procedure. Thus, if all other effects were absent then the differences would be equal. The main additional effect that should be considered is the increase in the level of steric hindrance when moving from dimethylamino-phosphazene to the more bulky pyrrolidino-phosphazene. This increase in steric hindrance reduces the possibility of solvation of the protonation centre of the protonated phosphazene molecule. The pattern of change of the normalized differences supports this qualitative interpretation: it is easy to see that the larger the solvent molecule, the smaller the normalized difference decreasing from 0.9 for the smallest solvent—H_2O—to 0.3 for the bulkiest solvent under consideration-THF.

Comparison of pK_a values of phosphazenes with other types of bases

If the pK_a values of the reference compounds (**19–23**) in water are examined (see Table 1 and Fig. 1), it can be pointed out that guanidines (**19**, **20**) are more basic than the phosphazenes under study. As for amines (**21**, **22**) and pyridine (**23**), the basicity of these compounds in water is "bracketed" between the pK_a values of phosphazenes. The situation is similar in AN and THF, but on an average the pK_a values of phosphazenes are slightly higher relative to the reference compounds. In the gas phase the situation is completely different from that in the condensed media: it is possible to clearly distinguish between two groups—phosphazenes and reference compounds. Phosphazenes are in the gas phase obviously more basic than guanidines, amines and pyridines in the reference group.

Another interesting point is to compare the basicities of the substituted PhP$_1$(pyrr) phosphazenes studied in this work with corresponding anilines. pK_a values of substituted anilines in water correlate well with the pK_a values of the respective substituted PhP$_1$(pyrr) phosphazenes in water: pK_a(Phosphazene) = 8.98 + 0.495pK_a(aniline); *s*(intercept) = 0.11, *s*(slope) = 0.03, $n = 12$, $r^2 = 0.960$, $S = 0.35$. As seen, the basicity of PhP$_1$(pyrr) phosphazenes is around two times less sensitive towards the substitution in the aromatic ring than the basicity of anilines. The corresponding correlation can be seen in Fig. 2.

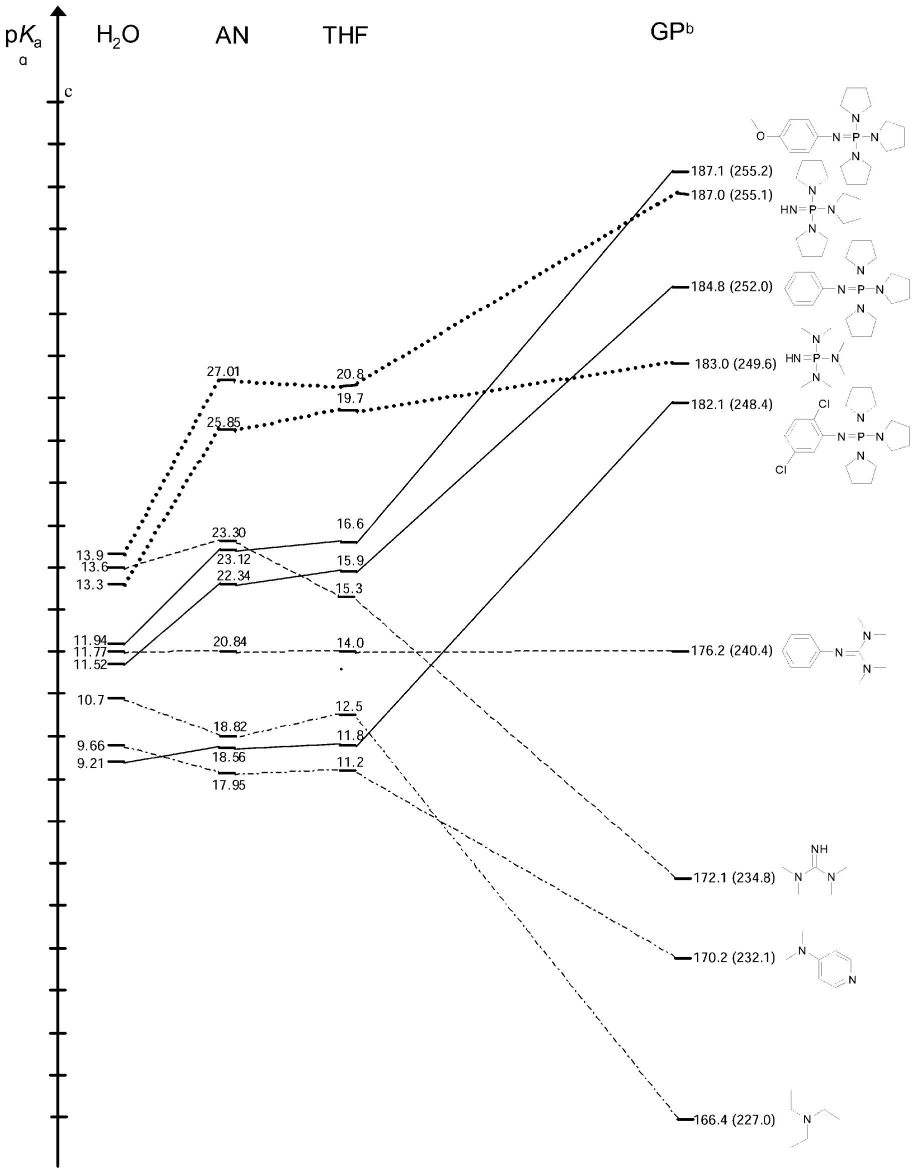

Fig. 1 Interrelations between basicities of bases belonging to different families in different media. [a]The absolute pK_a values in different media are not directly comparable, so phenyltetramethylguanidine (PhTMG) has been used as an arbitrary reference compound for placement of the scales on the figure. [b]The pK_a values for the gas phase (GP) are found according to the following equation pK_a(GP) = GB × 2.30/RT = GB/1.364. The gas-phase basicities (in kcal mol^{-1}) are given in brackets. [c]The pK_a arrow is divided into pK_a units but as the pK_a values in different media cannot be compared directly, the numbers were not added to the division markers.

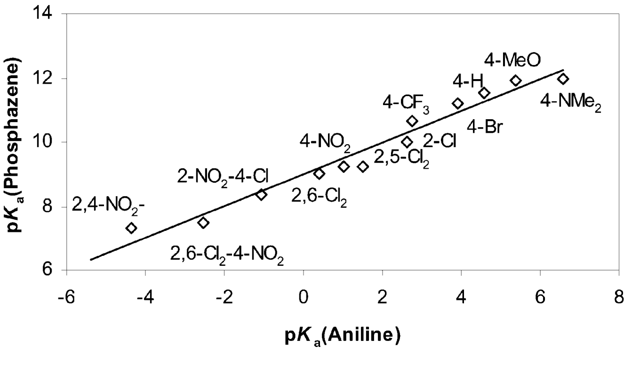

Fig. 2 Correlation of pK_a values in water of phenyl-substituted anilines and PhP$_1$(pyrr)phosphazenes. The pK_a values of anilines are from ref. 2, 19, 23.

It is of interest to compare the effect of the substitution of the imino-hydrogen by phenyl ring in tetramethylguanidine and in P$_1$(pyrr) and P$_1$(dma) phosphazenes. In all condensed media the basicity decreasing effect is larger in the phosphazenes (compare **3** and **17**; **5** and **18**) than in tetramethylguanidine, the effects being as follows: 2.3 (in water), 4.67 (in AN) and 4.8 (in THF) pK_a units for **17** and **3**; 2.64, 4.6 and 4.4 pK_a units for **18** and **5**; 1.83, 2.46 and 1.3 for **19** and **20** (the same order of solvents). The effects of substitution of the imino-hydrogen in guanidines has been thoroughly discussed[16] and the comparison of substituted imino-hydrogen in guanidines with phosphazenes is given in ref. 17, which also describes the basicity decrease. In the gas phase the substitution of the imino-H in tetramethylguanidine by a phenyl ring leads to a basicity increase, and in the phosphazenes to a

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small basicity decrease. These data for three different media allow us to generalize the earlier suggestion about the nature of the P=N double bond in phosphazenes. In a previous paper[1] it was proposed that this bond in phenyl P_1 pyrrolidino phosphazenes and in phenyl P_1 dimethylamino phosphazenes has a certain contribution from the ylidic (zwitterionic) structure. The basicity decreasing effects of the compounds studied in this work lead to the same conclusion.

Acknowledgements

This work was supported by the grants No 5800, 5508 and 6701 from the Estonian Science Foundation.

References

1 I. Kaljurand, T. Rodima, I. Leito, I. A. Koppel and R. Schwesinger, *J. Org. Chem.*, 2000, **65**, 6202–6208.
2 I. Kaljurand, A. Kütt, L. Sooväli, T. Rodima, V. Mäemets, I. Leito and I. A. Koppel, *J. Org. Chem.*, 2005, **70**, 1019–1028.
3 T. Rodima, I. Kaljurand, A. Pihl, V. Mäemets, I. Leito and I. A. Koppel, *J. Org. Chem.*, 2002, **67**, 1873–1881.
4 I. Kaljurand, T. Rodima, A. Pihl, V. Mäemets, I. Leito, I. A. Koppel and M. Mishima, *J. Org. Chem.*, 2003, **68**, 9988–9993.
5 A. A. Kolomeitsev, I. A. Koppel, T. Rodima, J. Barten, E. Lork, G.-V. Röschenthaler, I. Kaljurand, A. Kütt, I. Koppel, V. Mäemets and I. Leito, *J. Am. Chem. Soc.*, 2005, **127**, 17656–17666.
6 C. J. Drummond, F. Grieser and T. W. Healy, *J. Phys. Chem.*, 1988, **92**, 2604–2613.
7 C. Rottman and D. Avnir, *J. Am. Chem. Soc.*, 2001, **123**, 5730–5734.
8 S. K. Saha, S. Santra and S. K. Dogra, *J. Mol. Struct.*, 1999, **478**, 199–210.
9 Z. Yuanqin, L. Fan, L. Xiaoyan and L. Jing, *Talanta*, 2002, **56**, 705–710.
10 P. V. Jaiswal, V. S. Ijeri and A. K. Srivastava, *Colloids Surf., B*, 2005, **46**, 45–51.
11 T. Rodima, V. Mäemets and I. Koppel, *J. Chem. Soc., Perkin Trans. 1*, 2000, 2637–2644.
12 J. Tang, J. Dopke and J. G. Verkade, *J. Am. Chem. Soc.*, 1993, **115**, 5015–5020.
13 R. G. Bates, *Determination of pH. Theory and Practice*, Wiley, New York, 1973.
14 I. A. Koppel, J. B. Koppel, L. I. Muuga and V. O. Pihl, *Org. React.*, 1988, **25**(2), 131–146.
15 J. Steigman and D. Sussman, *J. Am. Chem. Soc.*, 1967, **89**, 6400–6406.
16 E. D. Raczynska, P.-C. Maria, J.-F. Gal and M. Decouzon, *J. Phys. Org. Chem.*, 1994, **7**, 725–733.
17 E. D. Raczynska, M. K. Cyranski, M. Gutowski, J. Rak, J.-F. Gal, P.-C. Maria, M. Darowska and K. Duzmal, *J. Phys. Org. Chem.*, 2003, **16**, 91–106.
18 E. D. Raczynska, M. Decouzon, J.-P. Gal, P.-C. Maria, K. Wozniak, R. Kurg and S. N. Carins, *Trends Org. Chem.*, 1998, **7**, 95–103.
19 D. D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solution: Published as a Supplement to Pure and Applied Chemistry*, Butterworth, London, 1965.
20 I. M. Kolthoff, M. K. Chantooni, Jr. and S. Bhowmik, *J. Am. Chem. Soc.*, 1968, **90**, 23–28.
21 E. P. L. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data*, 1998, **27**, 413–656.
22 *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*, ed. V. Palm, Vinity, Moscow-Tartu, 1975–1985.
23 O. Pytela, J. Kulhanek, E. Jiraskova and T. Nevecna, *Collect. Czech. Chem. Commun.*, 2001, **66**, 1638–1658.