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Extension of the Self-Consistent Spectrophotometric Basicity Scale in Acetonitrile to a Full Span of 28 pK_a Units: Unification of Different Basicity Scales

Ivari Kaljurand, Agnes Kütt, Lilli Sooväli, Toomas Rodima, Vahur Mäemets, Ivo Leito,* and
Ilmar A. Koppel

Department of Chemistry, University of Tartu, Jakobi 2, 51014 Tartu, Estonia

ivo.leito@ut.ee

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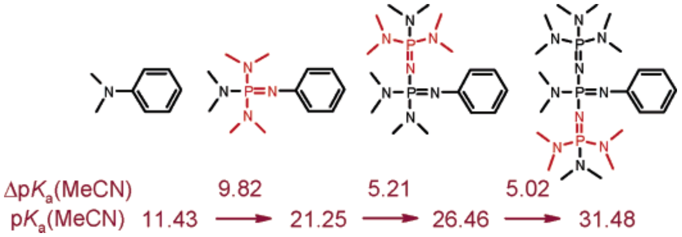

The earlier compiled self-consistent spectrophotometric basicity scale in acetonitrile (AN) was expanded to range from 3.8 to 32.0 pK_a units, that is 28 orders of magnitude. Altogether 54 new relative basicity measurements (ΔpK_a measurements) were carried out and 37 new compounds were introduced to the scale (it now includes altogether 89 bases). The relative basicity of any two bases in the scale can be obtained by combining at least two independent sets of measurements. Multiple overlapping measurements make the results more reliable. The overall consistency (as defined earlier) of the measurements is $s = 0.03$ pK_a units. Thorough analysis of all of our experimental data (ΔpK_a values of this and earlier works) and experimental pK_a data in AN available in the literature (works from the groups of Coetzee and Padmanabhan, Kolthoff and Chantooni, Jr., the Schwesinger group, Bren' et al. and some others, altogether 19 papers) was carried out. On the basis of this analysis the anchor point of the scale—pyridine—was shifted upward by 0.20 pK_a units thereby also revising the absolute pK_a values of all the bases on the scale. This way very good agreement between our relative data and the absolute pK_a values of the abovementioned authors was obtained. The revised basicity scale was interconnected with the earlier published self-consistent acidity scale by ΔpK_a measurements between acids and bases. The rms deviation between the directly measured ΔpK_a values and the absolute pK_a values of the compounds was 0.10 pK_a units.

Introduction

Measuring the base strength is a natural part of studies related to strong bases. One of the most widely used solvents for measurements of basicities of strong bases is acetonitrile (AN). Despite the contributions from several groups, (especially the Schwesinger,[1,2] Sundermeyer,[3] and Verkade[4] groups), the data on basicity in AN in the region of DBU and above continue to be scarce in the literature. In some cases, the information about the basicity of several superstrong bases (ca. pK_a(AN) > 33) is based on the extrapolations using the respective data in another dipolar aprotic solvent, DMSO.[2,4,5] Most importantly, what is missing, is a self-consistent scale of base strength in that strongly basic region. In previous publications we have established self-consistent spectrophotometric basicity scale in AN medium.[6,7] That scale spans over 17 pK_a units and covers significant part of

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* To whom correspondence should be addressed. Phone: +372 7 375 259. Fax: +372 7 375 264.

[1] Schwesinger, R.; Willaredt, J.; Schlemper, H.; Keller, M.; Schmitt, D.; Fritz, H. *Chem. Ber*. **1994**, *127*, 2435−2454.

[2] Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; Putzas, D.; Rotter, H. W.; Bordwell, F. G.; Satish, A. V.; Ji G.-Z.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Walz, L. *Liebigs Ann*. **1996**, 1055−1081 and references therein.

[3] Raab, V.; Kipke, J.; Gschwind, R. M.; Sundermeyer, J. *Chem. Eur. J.* **2002**, *8*, 1682−1693 and references therein.

[4] Verkade, J. G. *Top. Curr. Chem.* **2003**, *223*, 1−44 and references therein.

[5] Schwesinger, R. *Nachr. Chem. Technol. Lab.* **1990**, *38,* 1214−1226 and references therein.

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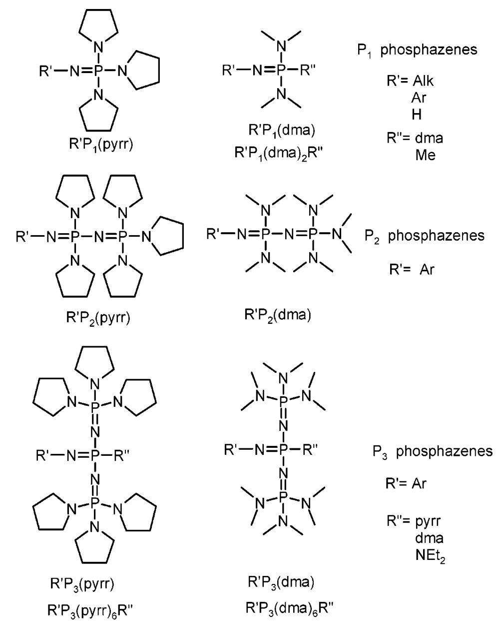
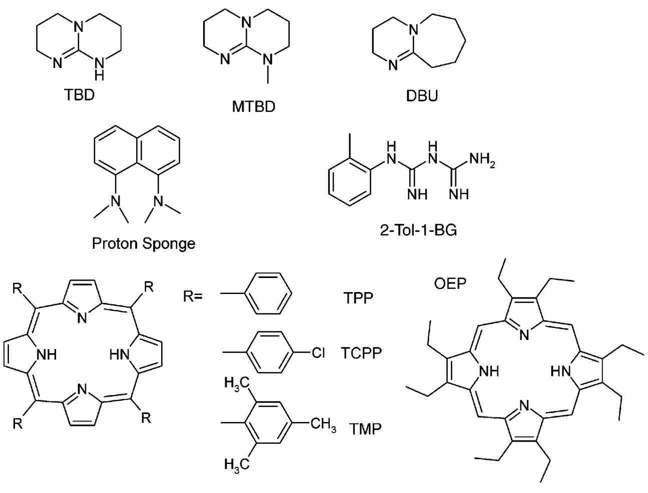
SCHEME 1



SCHEME 2



basicity range in AN from 2-chloropyridine ($pK_a = 6.60$) to DBU ($pK_a = 24.13$).

The primary goal of our present work is to expand significantly the existing self-consistent scale toward superbasic direction and also toward weaker neutral organic bases for several pK_a units. The extension of the scale adds many new important compounds (see Schemes 1 and 2).

Second, due to the abundant new data, we are now in the position to critically review the absolute basicity values assigned to the bases in our earlier works using pyridine as the reference base.[6-8] We will now compare our data with the data of 13 different research groups. On the basis of this comparison, we can shift the reference point of our scale (which is a relative scale, see ref 6) and reassign new absolute values to the compounds in such a way that the agreement between our data and the data of the other authors is the best possible.

Basicity of a base B in solvent S is defined using eq 1 and is expressed as dissociation constant K_a of the conjugate acid HB^+ of the base B or more commonly its negative logarithm pK_a.

$$HB^+ + S \rightleftarrows B + HS^+ \tag{1}$$

$$K_a = \frac{a(HS^+)a(B)}{a(HB^+)} \tag{2}$$

To exclude the necessity to measure the solvated hydrogen ion (HS^+) activity (its measurement is problematic in nonaqueous solvents) we studied the equilibrium between two bases B_1 and B_2:

$$B_2 + HB_1^{\ +} \rightleftarrows HB_2^{\ +} + B_1 \tag{3}$$

The relative basicity of the two bases B_1 and B_2 (ΔpK_a) is defined as follows:

$$\Delta pK_a = pK_a(HB_2^{\ +}) - pK_a(HB_1^{\ +}) = \log \frac{a(HB_2^{\ +})a(B_1)}{a(HB_1^{\ +})a(B_2)} \tag{4}$$

As can be seen the activity of HS^+ is excluded from the equation. The measurements were carried out using our previously developed method.[6,9] The method consists of UV−vis spectrophotometric titration of a solution, where both of the bases are present, with an optically transparent acid or base.

Experimental Section

Chemicals. Synthesis, purification, and identification of previously used noncommercial phospahazene bases is described in refs 8 and 10. Other commercial bases were purified using standard methods when needed, and taking extra care to minimize compounds exposure to air and humidity during and after purification. Details are given in the Supporting Information. Neutral acids (Table 2) were the same as used earlier.[9]

UV−vis spectral purity of all the bases for the present work was checked by following the change in UV−vis spectra on the titration of solution of the pure base with an acid. For all compounds having isosbestic points in the wavelength range that was used for calculations, the isosbestic points were sharp. This indicates the spectral purity of the compounds.

Solutions of trifluoromethanesulfonic acid (TfOH) (99+%) as acidic titrant and $EtP_2(dma)$ (>98%), $EtP_1(pyrr)$ (**8**), or triethylamine (99%) (**34**) as basic titrant were the same as used earlier.[6−8] The solution of $EtP_2(dma)$ was made fresh daily and used within 8 h after preparation as it reacts slowly with acetonitrile. Other solutions were used within 36 h after preparation.

Commercial AN with water concentration stated by producer below 0.005% (determined in our lab by coulometric Karl Fischer titration below 0.0040%) was used.

4-NO$_2$-C$_6$H$_4$P$_1$(pyrr) (38). To the suspension of 2.2 g (8 mmol) of $4\text{-}NO_2\text{-}C_6H_4NPCl_3$[11] in 40 mL of dry benzene and 6

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[6] Kaljurand, I.; Rodima, T.; Leito, I.; Koppel, I.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 6202−6208.

[7] Inamo, M.; Kohagura, T.; Kaljurand, I.; Leito, I. *Inorg. Chim. Acta* **2002**, *340*, 87−96.

[8] Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. *J. Org. Chem.* **2002**, *67*, 1873−1881.

[9] Leito, I.; Kaljurand, I.; Koppel, I. A.; Yagupolskii, L. M.; Vlasov, V. M. *J. Org. Chem.* **1998**, *63*, 7868−7874.

[10] Kaljurand, I.; Rodima, T.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I.; Mishima, M. *J. Org. Chem.* **2003**, *68*, 9988−9993.

[11] Zhmurova, I. N.; Kirsanov, A. V. *J. Gen. Chem. USSR (Engl. Trans.)* **1960**, *30*, 3018−3029.

TABLE 1. Continuous Self-Consistent Basicity Scale of Neutral Bases in Acetonitrile

	Base	pK_a(AN)^b
1	4-MeO-$C_6H_4P_3$(dma)	**31.99**
2	PhP_3(dma)	**31.48**
3	2-Cl-$C_6H_4P_3$(pyrr)$_6$NEt$_2$	**31.19**
4	4-CF$_3$-$C_6H_4P_3$(pyrr)	**30.50**
5	2-Cl-$C_6H_4P_3$(dma)$_6$NEt$_2$	**30.16**
6	2,5-Cl$_2$-$C_6H_3P_3$(pyrr)$_6$NEt$_2$	**29.16**
7	4-CF$_3$-$C_6H_4P_3$(dma)	**29.10**
8	EtP$_1$(pyrr)	**28.88**
9	t-BuP$_1$(pyrr)	**28.42**
10	4-MeO-$C_6H_4P_2$(pyrr)	**28.23**
11	PhP$_2$(pyrr)	**27.55**
12	MeP$_1$(dma)	**27.52**
13	HP$_1$(pyrr)	**27.01**
14	t-BuP$_1$(dma)	**26.98**
15	PhP$_2$(dma)	**26.46**
16	TBD	**26.03**
17	HP$_1$(dma)	**25.85**
18	MTBD	**25.49**
19	2-Cl-$C_6H_4P_2$(pyrr)	**25.42**
20	DBU	**24.34**
21	4-NMe$_2$-$C_6H_4P_1$(pyrr)	**23.88**
22	4-MeO-$C_6H_4P_1$(pyrr)	**23.12**
23	PhP$_1$(pyrr)	**22.34**
24	PhP$_1$(dma)	**21.25**
25	4-Br-$C_6H_4P_1$(pyrr)	**21.19**
26	PhP$_1$(dma)$_2$Me	**21.03**
27	PhTMG	**20.84**
28	1-NaphtP$_1$(pyrr)	**20.61**
29	2-Cl-$C_6H_4P_1$(pyrr)	**20.17**
30	4-CF$_3$-$C_6H_4P_1$(pyrr)	**20.16**
31	2-Tol-1-BG	**19.66**
32	pyrrolidine	**19.56**
33	2-Cl-$C_6H_4P_1$(dma)	**19.07**
34	Et$_3$N	**18.82**
35	Proton Sponge	**18.62**
36	2,6-Cl$_2$-$C_6H_3P_1$(pyrr)	**18.56**
37	2,5-Cl$_2$-$C_6H_3P_1$(pyrr)	**18.52**
38	4-NO$_2$-$C_6H_4P_1$(pyrr)	**18.51**
39	4-Pyrr-Pyridine	**18.33**
40	4-NMe$_2$-Pyridine	**17.95**
41	2-NO$_2$-4-Cl-$C_6H_3P_1$(pyrr)	**17.68**
42	4-NH$_2$-Pyridine	**17.62**
43	2-NO$_2$-5-Cl-$C_6H_3P_1$(pyrr)	**17.27**
44	PhCH$_2$NH$_2$	**16.91**
45	2-NO$_2$-4-CF$_3$-$C_6H_3P_1$(pyrr)	**16.54**
46	2-NH$_2$-Acridine	**16.39**
47	2-NH$_2$-1-Me-Benzimidazole	**16.31**
48	2-NH$_2$-Benzimidazole	**16.08**
49	2,3-(NH$_2$)$_2$-Pyridine	**15.24**
50	2,4,6-Me$_3$-Pyridine	**14.98**
51	2,4-(NO$_2$)$_2$-$C_6H_3P_1$(pyrr)	**14.88**
52	2,6-(NH$_2$)$_2$-Pyridine	**14.77**

Directly measured ΔpK_a^{a}

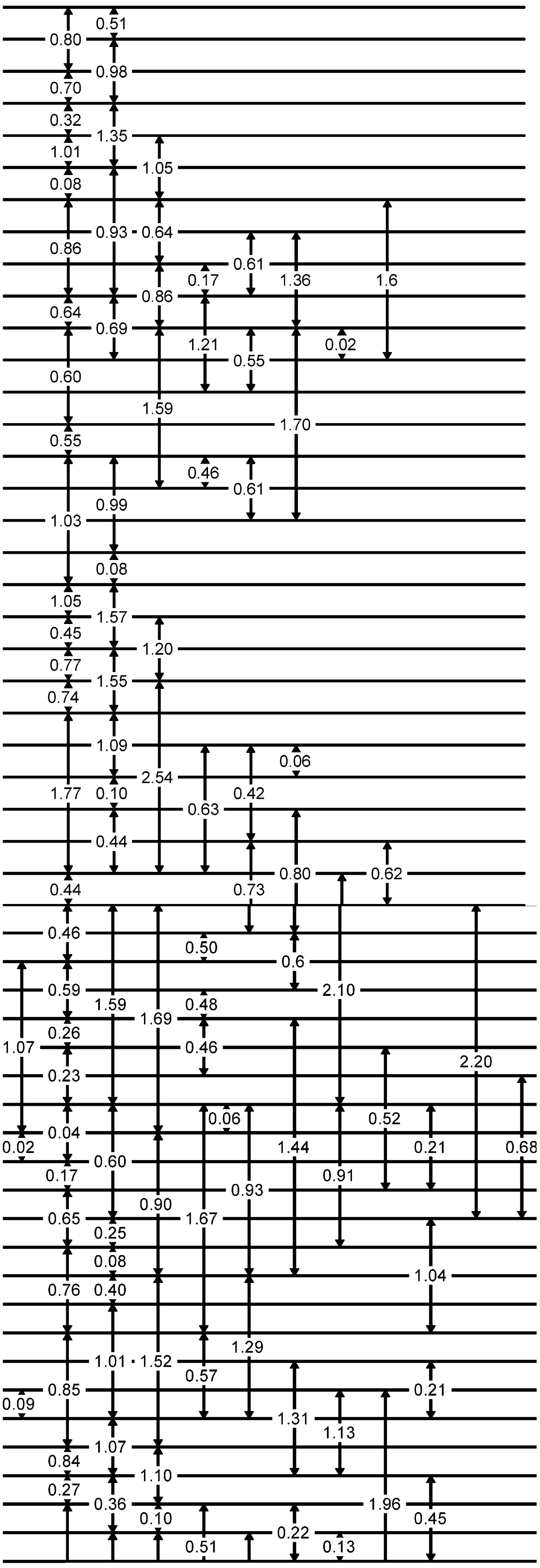
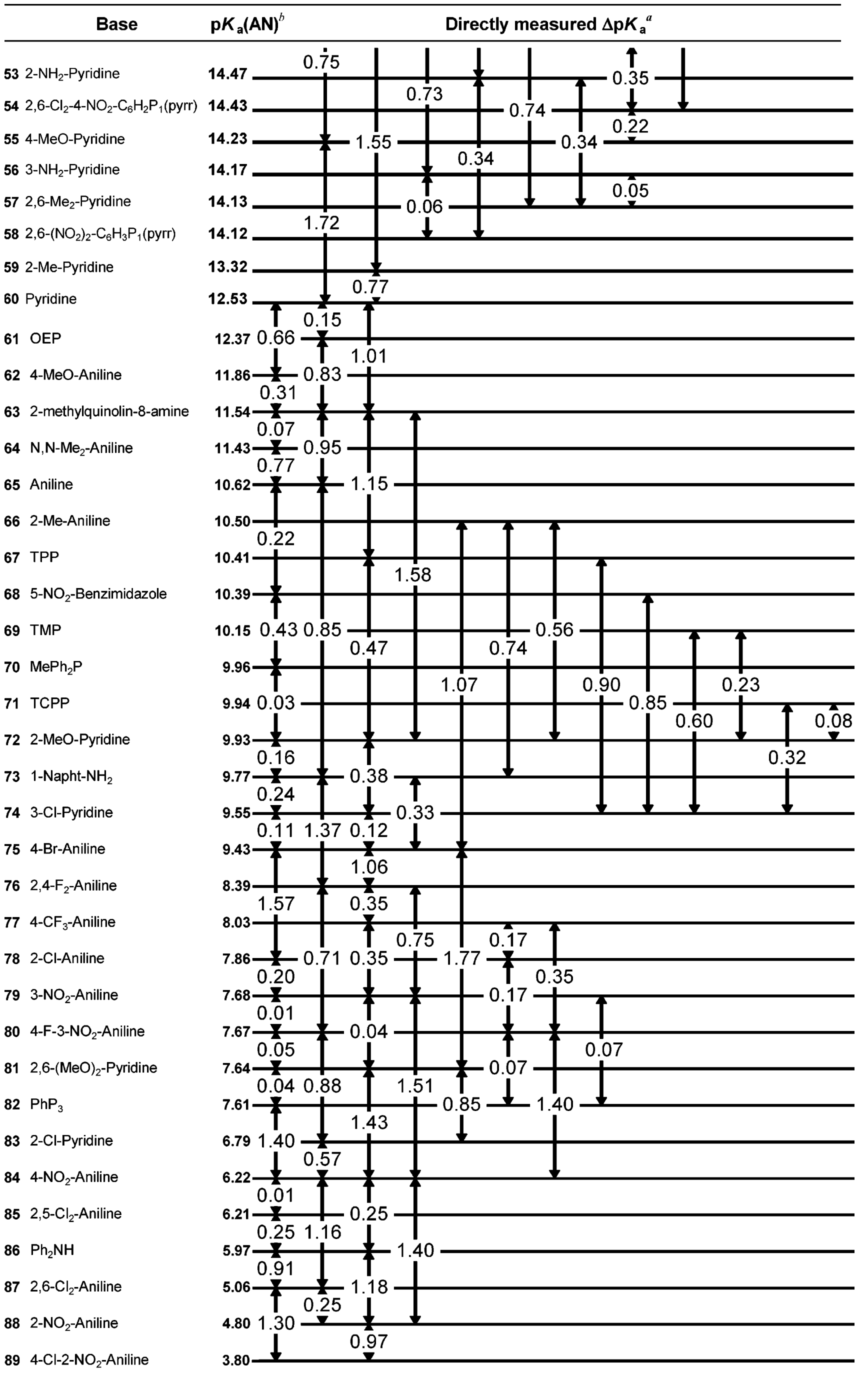


Table 1. (Continued)



	Base	pK_a(AN)[b]
53	2-NH_2-Pyridine	**14.47**
54	2,6-Cl_2-4-NO_2-$C_6H_2P_1$(pyrr)	**14.43**
55	4-MeO-Pyridine	**14.23**
56	3-NH_2-Pyridine	**14.17**
57	2,6-Me_2-Pyridine	**14.13**
58	2,6-$(NO_2)_2$-$C_6H_3P_1$(pyrr)	**14.12**
59	2-Me-Pyridine	**13.32**
60	Pyridine	**12.53**
61	OEP	**12.37**
62	4-MeO-Aniline	**11.86**
63	2-methylquinolin-8-amine	**11.54**
64	N,N-Me_2-Aniline	**11.43**
65	Aniline	**10.62**
66	2-Me-Aniline	**10.50**
67	TPP	**10.41**
68	5-NO_2-Benzimidazole	**10.39**
69	TMP	**10.15**
70	$MePh_2P$	**9.96**
71	TCPP	**9.94**
72	2-MeO-Pyridine	**9.93**
73	1-Napht-NH_2	**9.77**
74	3-Cl-Pyridine	**9.55**
75	4-Br-Aniline	**9.43**
76	2,4-F_2-Aniline	**8.39**
77	4-CF_3-Aniline	**8.03**
78	2-Cl-Aniline	**7.86**
79	3-NO_2-Aniline	**7.68**
80	4-F-3-NO_2-Aniline	**7.67**
81	2,6-$(MeO)_2$-Pyridine	**7.64**
82	PhP_3	**7.61**
83	2-Cl-Pyridine	**6.79**
84	4-NO_2-Aniline	**6.22**
85	2,5-Cl_2-Aniline	**6.21**
86	Ph_2NH	**5.97**
87	2,6-Cl_2-Aniline	**5.06**
88	2-NO_2-Aniline	**4.80**
89	4-Cl-2-NO_2-Aniline	**3.80**

[a] The numbers on the arrows are the experimental ΔpK_a values from this work and our previous works.[6-8] [b] Absolute pK_a values (see the Results).

mL of THF 3.48 g (48 mmol) of pyrrolidine solution in 9 mL of benzene was added at 50 °C. The mixture was stirred more an hour at 50–60 °C and left aside at +5 °C for a night. Pyrr·HCl was filtered off and solvent removed at reduced pressure. To the brown viscous residual (3.5 g) about 20 mL of 70% aqueous solution of $EtNH_2$ was added. The content of flask was stirred by means of glass stick. Separated yellow fine precipitate was filtered, washed with water and recrystallized from 1:4 mixture of $CHCl_3$/MeOH: yield 49% (1.5 g); mp 164.6–165.3 °C; ^1H NMR (200 MHz, THF) δ 1.8 (m, 12H, overlapped by solvent), 3.19 (dt, 12H, $J_{P-H} = 3.9$, $J_{H-H} = 6.6$), 6.60 (dd, 2H, $J_{P-H} = 0.6$, $J_{H-H} = 9.3$), 7.85 (dd, 2H, $J_{P-H} = 1.3$, $J_{H-H} = 9.3$); ^{13}C NMR (50 MHz, THF) δ 27.0 (d, $J_{C-P} = 7.8$), 47.5 (d, $J_{C-P} = 3.8$), 122.1 (d, $J_{C-P} = 19.3$), 125.7 (d, $J_{C-P} = 1.7$), 137.6, 161.5 (d, $J_{C-P} = 2.9$). Anal. Calcd for $C_{18}H_{28}N_5O_2P$: C, 57.28; H, 7.48; N, 18.56. Found: C, 57.28; H 7.54; N, 18.76.

Experimental Setup. The spectrophotometric titration method used in this work is mostly the same as described earlier.[6,8,9] Details are given in the Supporting Information.

Calculation Methods. The ΔpK_a values for the equilibria between bases of identical charge type (i.e., corresponding to

TABLE 2. Measurements of Neutral Acid−Cationic Acid Pairs in Acetonitrile[a]

acid (HA)	base (B)	ΔpK_a (from direct measurement)[b]	difference[c]
2,4-$(NO_2)_2C_6H_3OH$	2-NH_2-1-Me benzimidazole	0.23	0.12
3-CF_3-$C_6H_4CH(CN)_2$	2,4-$(NO_2)_2$-$C_6H_3P_1$(pyrr)	−0.25	0.09
3-CF_3-$C_6H_4CH(CN)_2$	2,3-$(NH_2)_2$-pyridine	−0.57	0.05
4-CH_3-$C_6F_4CH(CN)_2$	3-NH_2-pyridine	−0.36	0.07
		−0.34	0.05
4-CH_3-$C_6F_4CH(CN)_2$	2-Me-pyridine	0.58	−0.02
4-CH_3-$C_6F_4CH(CN)_2$	pyridine	1.33	0.02
$C_6F_5CH(CN)_2$	3-NH_2-pyridine	−1.23	0.07
$C_6F_5CH(CN)_2$	2-Me-pyridine	−0.28	−0.03
4-H-$C_6F_4CH(CN)_2$	2-Me-pyridine	−0.31	−0.03
4-H-$C_6F_4CH(CN)_2$	pyridine	0.42	0.03
$C_{10}F_7CH(CN)_2$	pyridine	−0.34	0.04
Tos_2NH	pyridine	−0.66	0.10
4-NO_2-$C_6H_4CH(CN)_2$	pyridine	−0.93	0.01
4-NO_2-$C_6H_4CH(CN)_2$	2-methylquinolin-8-amine	0.02	0.05
$(C_6H_5SO_2)_2NH$	pyridine	−1.15	−0.04
picric acid	pyridine	−1.57	0.04
		−1.55	0.02
4-CF_3-$C_6F_4CH(CN)_2$	2-MeO-pyridine	0.26	0.00
		0.23	0.03
4-CF_3-$C_6F_4CH(CN)_2$	3-Cl-pyridine	0.68	−0.04
3-NO_2-C_6H_4-SO_3H	2-Cl-pyridine	−0.31	0.28
4-NO_2-C_6H_4-SO_3H	2,6-$(MeO)_2$-pyridine	−1.02	0.09
4-NO_2-C_6H_4-SO_3H	2-Cl-pyridine	−0.33	0.25
		average difference (st. dev)	0.05 (0.08)
		rms difference	0.10

[a] Acid scale[9] anchored to the picric acid value (pK_a = 11.00[14]), base scale anchored to the corrected pyridine value (pK_a = 12.53). [b] ΔpK_a values were found according to eq 7, and assuming radius of ions 4 Å. [c] Difference = (pK_a(HA) − pK_a(BH^+)) − ΔpK_a, where the pK_a values are from the scales of bases and acids (see ref 9), respectively.

eq 3) were calculated similarly as described previously[6,9,12] from recorded UV−vis spectra. It is assumed that the ratio $f(HB^+)/f(B)$ is the same for both bases (see ref 12) then with bases (cationic acids) and the eq 4 transforms into the following form

$$\Delta pK_a = pK_a(HB_2^{\ +}) - pK_a(HB_1^{\ +}) = \log \frac{[HB_2^{\ +}][B_1]}{[HB_1^{\ +}][B_2]} \quad (5)$$

where the equilibrium concentrations of the species are square bracketed.

For the pairs of bases in which one member has small difference in the spectra of neutral and protonated form (e.g., alkylphosphazenes, bicyclic guanidines) we also used the calculation method[8] in which in addition to the spectra also exact amount of moles of the compounds in titration vessel and added titrant are taken into consideration for ΔpK_a calculations (see ref 8 for details). Generally, good agreement between these two different approaches was obtained. Every ΔpK_a value given in Table 1 is an average value for one titration experiment (i.e., average of ΔpK_a values calculated for each 5−20 additions of titrant) using either only one or several ΔpK_a calculation methods.

When calculating the relative acidity of a neutral and a cationic acid according to eq 6

$$HA + B \rightleftarrows A^- + BH^+ \quad (6)$$

then the assumption that the ratios of the activity coefficients are equal is not valid any more and the ΔpK_a value is

$$\Delta pK_a = \log \frac{[B][HA]}{[A^-][BH^+]} - 2\log f \quad (7)$$

where the following approximations are made: $f = f(A^-) = f(BH^+)$ and $f(B) = f(HA) = 1$. The value of log f was calculated using the Debye−Hückel equation[13]

$$\log f = -\frac{1.64Z^2\sqrt{J}}{1 + 0.48a\sqrt{J}} \quad (8)$$

where J is the ionic strength of the solution, Z is the charge of the ion, and a is the size parameter of the ion that was taken 4 Å. The log f is not very sensitive to this parameter.

Results

The results are presented in Table 1. Altogether 54 new relative basicity measurements were carried out and 37 new compounds were introduced to the scale. As a result, the self-consistent basicity scale in AN has together with our previous experiments the range from 3.8 to 32.0 pK_a units, which is slightly over 28 orders of magnitude. The pK_a values for individual bases were found similarly to previous works[9,6] by minimizing the sum of squares of differences between directly measured ΔpK_a values and the assigned pK_a values:

$$u = \sum_{i=1}^{n_m} \{\Delta pK_a^{\ i} - [pK_a(HB_2^{\ +}) - pK_a(HB_1^{\ +})]\}^2 \quad (9)$$

The sum is taken over all the measurements whereby $\Delta pK_a^{\ i}$ is the result of a relative acidity measurement of conjugated acids of bases HB_1^+ and HB_2^+ (HB_2^+ is the acid whose pK_a is higher). pK_a(HB_1^+) and pK_a(HB_2^+) are the absolute pK_a values for the two conjugate acids as found by the least squares procedure. The precision and

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(12) Leito, I.; Rodima, T.; Koppel, I. A.; Schwesinger, R.; Vlasov, V. M. *J. Org. Chem.* **1997**, *62*, 8479−8483.

(13) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45−92 and references therein.

the consistency of the results can be assessed using a standard deviation as defined by eq 10:

$$s = \sqrt{\frac{u}{n_m - n_c}} \qquad (10)$$

The whole spectrophotometric basicity scale in AN (this work and refs 6−8 and excluding cationic bases from ref 7) has in total number of measurements $n_m = 180$, number of pK_a's determined $n_c = 88$ and the consistency of measurements $s = 0.03$ (see ref 9 for explanations on s as the measure of consistency). The thorough analysis of all of our experimental data (this work and refs 6−8) and experimental pK_a data in AN available in the literature was carried out, and it leads us to the conclusion that we need to shift slightly the anchor point of our scale taken from literature and consequently revise the absolute pK_a values. For details and justification see the Discussion. The full basicity scale in AN, including all 89 compounds and all measurements from present and previous works is presented in Table 1. Cationic porphyrin bases[7] were excluded from the scale because they have different charge type from the rest of the bases.

The relative basicity of any two bases in the scale can be obtained by combining at least two independent sets of measurements. Multiple overlapping measurements make the results more reliable and help to estimate their self-consistency. Reversibility of protonation/deprotonation process of all bases was checked. All equilibria were reached within minutes and were stable.

Connecting pK_a Scales of Acids of Different Charge Type in AN. In a previous work[9] we have set up self-consistent acidity scale in AN. The scale spans for around 13 pK_a units (from pK_a = 3.75−16.66). The scales of acids (or more precisely neutral acids) and bases (in other words, cationic acids) are in fact subunits of one and the same common acidity scale. They have been treated separately because of the simplicity of calculating ΔpK_a values for acids of identical charge type. Proton-transfer reaction between neutral acid and neutral base according to eq 6 leads to the following equation for ΔpK_a

$$\Delta pK_a = pK_a(HA) - pK_a(HB^+) = \log\frac{a(HA)a(B)}{a(HB^+)a(A^-)} \qquad (11)$$

which is transformed to give eq 7.

We attempted in this work to connect the previously set up acidity scale with the basicity scale reported in this paper. ΔpK_a measurements between neutral and cationic acids were carried out. The results are presented in Table 2. The average difference between the directly measured ΔpK_a value and the differences calculated from the assigned values is 0.05 pK_a units. The rms (root mean square) difference is 0.10 pK_a units. In general, the individual differences are less than 0.10 pK_a units. The most deviating pairs of compounds are the 3- and 4-nitrobenzenesulfonic acids vs 2-chloropyridine. pK_a measurements with sulfonic acids in AN have some specific difficulties, first of all the rather localized negative charge on the anion and the necessity to use somewhat higher concentrations for the measurements (see ref 9 for details).

Leaving aside compounds with highly localized charges on the anionic or cationic form (out of the compounds that are involved in our measurements this first of all applies to sulfonic acids) the two scales can be considered satisfactorily interconnected. The interconnection has some uncertainty that is best estimated from the rms difference given above. This means that when the pK_a value of a compound is estimated from measurements with references of different charge type, an additional uncertainty of ca. 0.1 pK_a units (at standard deviation level) has to be taken into account.

Discussion

Anchoring the Scale. Our basicity scale in AN has been previously[6] anchored to the pK_a value of pyridine:, 12.33 determined by Coetzee and Padmanabhan.[21] In light of the new data obtained in this work it is now reasonable to reexamine this anchor point.

Available pK_a data in AN for the bases studied in this work have been collected in Table 3. There are seven major papers where pK_a values for bases in AN have been published: The paper on basicities of amines (including aniline and pyridine) by Coetzee and Padmanabhan,[21] the papers on basicities of weak bases by Kolthoff et al.,[40,44,48,49] the contribution from the Schwesinger group on simple alkylphosphazenes, amidines and guanidines,[1] substituted pyridines from Augustin-Nowacka and Chmurzynski,[33] pyridines and anilines from Pawlak et al.,[23,35] anilines from Bren' et al.,[37] and arylphosphazenes using ^{13}C and ^{1}H NMR from Rodima et al.[19] There are still some other contributions (refs 9, 18, 24, 27, 28 32, and 36) that contain less data. If we correlate the literature pK_a values from particular research group in AN with the values from our present and previous[6−8] works (anchor compound pyridine, pK_a value 12.33) we can make the following observations:

1. A correlation series of the present data with literature values from particular author(s) shows in some cases (works of Coetzee,[21] Kolthoff,[40,44,48,49] Bren',[37] Zvezdina,[32] Schwesinger,[1] and Augustin-Nowacka[33]) close to unity slope (deviation is less than 0.03 units), whereas others differ more significantly (more than 0.07 units) from unity (works of Pawlak,[23,35] Rodima[19]).

2. The same correlations show that in some cases (works of Coetzee,[21] Kolthoff,[40,44,48,49] Bren',[37] Zvezdina,[32] Schwesinger[1]) the standard deviations of the regression line are small (less than 0.17 pK_a units), whereas in some cases (works of Pawlak,[23,35] Augustin-Nowacka,[33] Rodima[19]) the standard deviations of the regression line are larger (more than 0.23 pK_a units).

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(14) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 4428−4436.

(15) (a) Kovačević, B.; Maksić, Z. B. *Chem. Eur. J.* **2002**, *8*, 1694−1702. (b) Kovačević, B.; Maksić, Z. B. *Org. Lett.* **2001**, *3*, 1523−1526. (c) Kovačević, B.; Barić, D.; Maksić, Z. B. *New J. Chem.* **2004**, *28,* 284−288.

(16) *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*; Palm, V., Ed.; VINITI: Moscow-Tartu, 1975−1985.

(17) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 3, 413−656.

(18) Leffek, K.; Przuszynski, P.; Thanapaalasingham, K. *Can. J. Chem.* **1989**, *67*, 590−595.

(19) Rodima, T.; Mäemets, V.; Koppel, I. A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2637−2466.

(20) Przuszynski, P. *Can. J. Chem.* **1987**, *65*, 626−629.

(21) Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005−5010.

TABLE 3. Basicity Data of the Studied Bases Reported in the Literature

no.	base	pK_a values in AN	theor pK_a values in AN[a]	pK_α values in THF[b,c]	pK_a values in DMSO[d,e]	pK_a values in H_2O[a,d]	GB (kcal/mol)[b,f]
1	4-MeO-$C_6H_4P_3$(dma)			24.0			
2	PhP_3(dma)			23.5			
3	2-Cl-$C_6H_4P_3$(pyrr)$_6$$NEt_2$			22.0			
4	4-CF_3-$C_6H_4P_3$(pyrr)			23.1			
5	2-Cl-$C_6H_4P_3$(dma)NEt_2			20.8			
6	2,5-Cl_2-$C_6H_3P_3$(pyrr)$_6$$NEt_2$			20.2			
7	4-CF_3-$C_6H_4P_3$(dma)			21.7			
8	EtP_1(pyrr)	28.89[g]	28.8	21.7			
9	t-BuP_1(pyrr)	28.35[g]		20.2			
10	4-MeO-$C_6H_4P_2$(pyrr)			21.5			
11	PhP_2(pyrr)			20.9			
12	MeP_1(dma)	27.55[g]		20.7			252.2
13	HP_1(pyrr)			20.8			
14	t-BuP_1(dma)	26.88[g]	27.2	18.9	15.7[e]		253.2
15	PhP_2(dma)			19.8			
16	TBD	25.98[g]	26.2	21.0			244.3
17	HP_1(dma)		25.7	19.7			250.0
18	MTBD	25.44[g]	25.7	17.9			246.2
19	2-Cl-$C_6H_4P_2$(pyrr)			17.5			
20	DBU	24.33,[g] 23.9[h]		16.8	13.9[e]		242.7
21	4-NMe_2-$C_6H_4P_1$(pyrr)	23.9[i]		17.3			
22	4-MeO-$C_6H_4P_1$(pyrr)	23.4[i]		16.8			255.2
23	PhP_1(pyrr)	22.6[i]	22.8	16.0			252.0
24	PhP_1(dma)	20.9[i]	20.6	15.3			
25	4-Br-$C_6H_4P_1$(pyrr)	21.0[i]		15.3			
26	PhP_1(dma)$_2$Me			15.5			
27	PhTMG	20.6[h]	21.1	14.0		12.18[j]	240.4
28	1-$NaphtP_1$(pyrr)	20.7[i]		14.2			251.1
29	2-Cl-$C_6H_4P_1$(pyrr)	19.8[i]		13.2			251.1
30	4-CF_3-$C_6H_4P_1$(pyrr)			14.6			
32	pyrrolidine	19.58[k]		13.5	10.8	11.27[l]	218.8
33	2-Cl-$C_6H_4P_1$(dma)			12.5			
34	Et_3N	18.46,[k] 17.24[m]		12.5[n]	9.0[o],[p]	10.7	227.0
35	Proton Sponge (DMAN)	18.70,[q] 18.50,[r] 18.18[s]	19.9	11.1	7.5[t]	12.1[u]	238.0
36	2,6-Cl_2-$C_6H_3P_1$(pyrr)	18.0[i]		11.8			
37	2,5-Cl_2-$C_6H_3P_1$(pyrr)	17.9[i]		11.9			248.4
40	4-NMe_2-Pyridine (DMAP)	18.18[w]		11.2		9.60[j]	232.1
41	2-NO_2-4-Cl-$C_6H_3P_1$(pyrr)	17.5[i]		10.8			
42	4-NH_2-pyridine	17.61,[v] 18.38,[w] 17.00[x,y]				9.12	226.5
43	2-NO_2-5-Cl-$C_6H_3P_1$(pyrr)			10.1			
44	$PhCH_2NH_2$	16.76[k]			4.15	9.3	210.2
45	2-NO_2-4-CF_3-$C_6H_3P_1$(pyrr)			9.6			
46	2-NH_2-acridine					5.84	
48	2-NH_2-benzimidazole	15.95[v]				7.51	
49	2,3-$(NH_2)_2$-pyridine					6.7	
50	2,4,6-Me_3-pyridine	14.38[z]		8.1		7.45	
51	2,4-$(NO_2)_2$-$C_6H_3P_1$(pyrr)	14.5[i]		8.0			
52	2,6-$(NH_2)_2$-pyridine					6.00	
53	2-NH_2-pyridine	14.66,[w] 14.43[v]				6.75	218.8
54	2,6-Cl_2-4-NO_2-$C_6H_2P_1$(pyrr)			7.8			
55	4-MeO-pyridine			7.3		6.55	222.2
56	3-NH_2-pyridine	14.35[w]				6.04	220.5
57	2,6-Me_2-pyridine	14.41[w]		7.2	4.46	6.70	222.5
58	2,6-$(NO_2)_2$-$C_6H_3P_1$(pyrr)			7.5			
59	2-Me-pyridine	13.88,[w] 12.76[z]		6.3	4.01	5.94	219.2
60	pyridine	12.33,[k] 12.60,[w] 12.52[m]		5.5	3.4[o]	5.25	214.7
62	4-MeO-aniline	12.05[aa]		6.5		5.36	207.6
64	*N*,*N*-Me_2-aniline	12.30[y]		4.9	2.51[ab]	5.07[ac]	217.3
65	aniline	10.56,[k] 10.7,[ad] 10.57[aa]	10.9	5.2	3.72,[ab] 3.6[o]	4.62[ae]	203.3
66	2-Me-aniline			5.1		4.44	205.3
68	5-NO_2-benzimidazole					3.48	
70	$MePh_2P$	9.6[n]		6.4[n]			224.6
72	2-MeO-pyridine	10.60[y]		2.6		3.06	215.8
73	1-Napht-NH_2	11.10[y]				3.92[af]	209.2
74	3-Cl-pyridine	10.13,[m] 10.01[w]				2.84	208.3
75	4-Br-aniline	9.39[aa]		4.0		3.89	
76	2,4-F_2-aniline						
77	4-CF_3-aniline	8.16[aa]				2.75[ag]	
78	2-Cl-aniline					2.64[ae]	
79	3-NO_2-aniline	7.79,[aa] 7.60[ah]			1.15,[ai] 1.32	2.466[ac]	
80	3-NO_2-4-F-aniline					2.36[aj]	
81	2,6-$(MeO)_2$-pyridine					1.6	
82	Ph_3P	8.0[n]				2.7[n]	224.8
83	2-Cl-pyridine	7.76,[m] 6.80[w]				0.49	208.0
84	4-NO_2-aniline	6.21[aa]			−0.73[p]	1.00	199.4
85	2,5-Cl_2-aniline					1.53	
86	Ph_2NH					0.79[ak]	
87	2,6-Cl_2-aniline					0.42	
88	2-NO_2-aniline	4.85,[al] 4.95,[am] 5.30[an]			−1.76[p]	−0.20	

[a] Reference 15. [b] Reference 10. [c] Reference 8, some with minor corrections. [d] Reference 16. [e] Reference 2. [f] Reference 17. [g] Reference 1. [h] Reference 18. [i] Reference 19. [j] Reference 20. [k] Reference 21. [l] Reference 22. [m] Reference 23. [n] Reference 24. [o] Reference 25. [p] Reference 26. [q] Reference 27. [r] Reference 28. [s] Reference 29. [t] Reference 30. [u] Reference 31. [v] Reference 32. [w] Reference 33. [x] Reference 34. [y] Reference 35. [z] Reference 36. [aa] Reference 37. [ab] Reference 38. [ac] Reference 39. [ad] Reference 40. [ae] Reference 41. [af] Reference 42. [ag] Reference 43. [ah] Reference 44. [ai] Reference 45. [aj] Reference 46. [ak] Reference 47. [al] Reference 48. [am] Reference 49. [an] Reference 9. [ao] Reference 50. [ap] Reference 51.

These two observations lead to the following conclusions. First, the pK_a values from particular group that give in correlation of our data regression line with slope close to unity give confidence, that our scale has no contraction/expansion due to the different experimental conditions (temperature, composition of medium, effects arising from impurities, ionic association etc). Second, as our basicity scale is self-consistent by its nature, the pK_a values from a particular group that give on correlation with our results regression lines with relatively small standard deviations are truly close to self-consistency by themselves and can thus be considered reliable.

Thus, the experiments by Coetzee,[21] Kolthoff,[40,44,48,49] Bren',[37] Zvezdina,[32] and Schwesinger[1] for measurement of pK_a values can be considered to be carried out at nearly the same conditions as ours and are self-consistent. These works have altogether 26 common pK_a values of bases with our work (compounds **8**, **9**, **12**, **14**, **16**, **18**, **20**, **32**, **34**, **42**, **44**, **48**, **53**, **60**, **62**, **65**, **75**, **77**, **79**, **84**, **88**, and **89**). In addition, there are two works[27,28] that both have only one common compound (**35**) with our scale, but for which we are not able to find a reason to leave these values out from sample. The overall correlation of all these literature pK_a values with our pK_a values anchored to the pK_a value of pyridine 12.33 gives the following equation:

$$\mathrm{p}K_a(\text{literature}) = 0.25 + 0.995\mathrm{p}K_a(\text{this work}) \quad (12)$$

$$n = 28;\ s(\text{intercept}) = 0.05;\ s(\text{slope}) = 0.003;\ r^2 = 1.000;\ S = 0.11$$

The average value of our pK_a values (scale anchored to pyridine pK_a value 12.33) of the range what has common part with literature pK_a values is 16.14 pK_a units. At this point the difference between the hypothetical literature pK_a value described by the regression line and our average value is 0.18 pK_a units. The difference of hypothetical literature pK_a value at our anchor point value (pyridine, pK_a 12.33) described by the regression line and our value (12.33) is 0.19 pK_a units. We see, that these two approaches yield virtually identical corrections. Hence, we have corrected all our values increasing them by 0.20 pK_a units. The resulting corrected pK_a values of the bases are indicated in the Table 1.

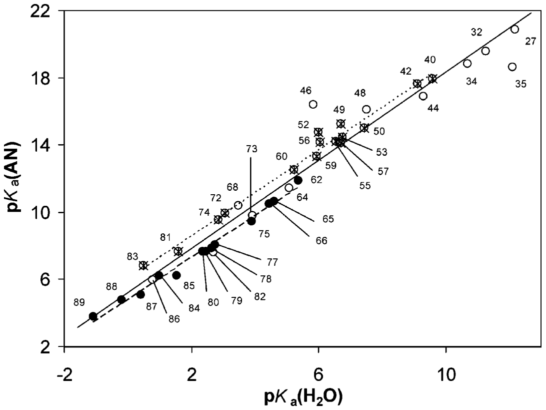

FIGURE 1. Correlation of the basicities of the studied bases in water and acetonitrile. Solid line corresponds to overall correlation; dotted line corresponds to pyridines and dashed line corresponds to anilines. Overall correlation: pK_a(AN) = 5.20 + 1.313pK_a(H$_2$O); s(intercept) = 0.27, s(slope) = 0.045, n = 40, r^2 = 0.957, S = 0.98.

Anilines. Correlation of the pK_a values in AN and water yields the following equation: pK_a (AN) = 4.78 + 1.246pK_a(H$_2$O); s(intercept) = 0.12, s(slope) = 0.042, n = 13, r^2 = 0.988, S = 0.28. Similar slope has been earlier found in correlation with cationic acids[27] and pyridines.[33] This means, that water has similar leveling ability for different groups of compounds. Basicity of anilines is more sensitive toward substitution in the aromatic ring in AN than in water (Figure 1).

If the data for compounds that have strong resonance acceptor substituents at the 2 or 4 position (i.e., 84, 88, and 89) are excluded from the correlation, then a better correlation line is obtained: pK_a (AN) = 4.29 + 1.379pK_a(H$_2$O); s(intercept) = 0.11, s(slope) = 0.034, n = 10, r^2 = 0.995, S = 0.15. The compounds with acceptor substituents have H$_2$O basicities progressively deviating from this line: by −0.40, −0.57 and −0.72 pK_a units, respectively. This situation is similar to the one described for neutral acids and interpreted in terms of the SSAR (substituent solvation assisted resonance) effect in the deprotonated forms of acids.[52,53] The SSAR effect is

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(22) Searles, S.; Tamres, M.; Block, F.; Quarterman, L. A. *J. Am. Chem. Soc.* **1956**, *78*, 4917−4920.

(23) Pawlak, Z.; Zundel, G.; Fritsch, J.; Wawrzynów, A.; Kuna, S.; Tusk, M. *Electrochim. Acta* **1984**, *29*, 391−395.

(24) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155−9171.

(25) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23−28.

(26) Cook, A. G.; Mason, G. W. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2579−2588.

(27) Koppel, I. A.; Koppel, J. B.; Pihl, V. O. *Org. React.* **1987**, *24*, 387−398.

(28) Pozharskii, A. F.; Chikina, N. L.; Vistorobskii, N. V.; Ozeryanskii, V. A. *Russ. J. Org. Chem.* **1997**, *33*, 1810−1813.

(29) Kurasov, L. A.; Pozharskii, A. F.; Kuzmenko, V. V. *Zh. Org. Khim.* **1983**, *19*, 859−864.

(30) Llamas-Saiz, A. L.; Foces-Foces, C.; Elguero, J. *J. Mol. Struct.* **1994**, *328*, 297−323 and references therein.

(31) Hibbert, F. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1862−1866.

(32) Zvezdina, E. A.; Zdanova, M. P.; Bren', V. A.; Dorofeenko, G. N. *Zh. Geterotsikl. Soedineii* **1974**, *11*, 1461−1467.

(33) Augustin-Nowacka, D.; Chmurzyński, L. *Anal. Chim. Acta* **1999**, *381*, 215−220.

(34) Pawlak, Z. *J. Chem. Termodyn.* **1987**, *19*, 443−447.

(35) Pawlak, Z.; Urbanczyk, G. *J. Mol. Struct.* **1988**, *177*, 401−406.

(36) Zdanov, J. A.; Bren', V. A.; Alekseeva, V. G.; Alekseev, J. E.; Fomina, V. N. *Dokl. Akad. Nauk SSSR* **1974**, *219*, 108−110.

(37) Bren', V. A.; Maloesheva, E. N.; Minkin, V. I. *Org. React* **1967**, *4*, 534−555.

(38) Benoit, R. L.; MacKinnon, M. J.; Bergeron, L. *Can. J. Chem.* **1981**, *59*, 1501−1504.

(39) Fickling, M. M.; Fischer, A.; Mann, B. R.; Packer, J.; Vaughan, J. *J. Am. Chem. Soc.* **1959**, *81*, 4226−4230.

(40) Kolthoff, I. M.; Chantooni, M., Jr.; Bhowmik, S. *Anal. Chem.* **1967**, *39*, 1627−1633.

(41) Pytela, O.; Otypeka, M.; Kulhanek, J.; Otypekova, E.; Nevecna, T. *J. Phys. Chem. A*, **2003**, *107*, 11489−11496.

(42) Bryson, A. *J. Am. Chem. Soc.* **1960**, *82*, 4862−4871.

(43) Sheppard, W. A. *J. Am. Chem. Soc.* **1963**, *84*, 1314−1318.

(44) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 3320−3326.

(45) Wolford, R. K. *J. Phys. Chem.* **1964**, *68*, 3392−3398.

(46) Greenbaum, S. B. *J. Am. Chem. Soc.* **1955**, *77*, 3221−3224.

(47) Paul M. A. *J. Am. Chem. Soc.* **1954**, *76*, 3236−3239.

(48) Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 3927−3935.

(49) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 4768−4769.

(50) Pytela, O.; Kulhanek, J.; Jiraskova, E.; Nevecna, T. *Collect. Czech. Chem. C.* **2001** *66* (11), 1638−1658.

(51) Kolthoff, I. M.; Ikeda, S. *J. Phys. Chem.* **1961**, *83*, 1020−1026.

probable in this case also: H_2O is a better electrophilically solvating solvent for the NO_2 group in neutral anilines than AN. The correlation between the gas-phase basicities of anilines and the respective AN data would be especially interesting from this point of view, because it is reasonable to expect that the SSAR effect is better visible on going from the gas phase to the solvent. However, the protonation chemistry of anilines in the gas phase is more complicated than in solution. Some substituted anilines (and possibly aniline itself) have different protonation sites in the gas phase than they do in the solution phase.[54] In solution, anilines protonate on the amino group. In the gas phase for some of the anilines, besides N-protonation the protonation on the substituent or ring protonation has been suggested. First of all those that contain strong electron-acceptor substituents, such as nitro, cyano, etc. in the ortho or para position are believed to protonate on that substituent, at the same time in the case of meta-substituted anilines the amino group is the preferred site of protonation.[55b] The discussion on the protonation site of the unsubstituted aniline is still ongoing. Computational results have been giving contradictory information, both in favor of amino protonation[56] and ring protonation.[55] Most likely in the gas phase both protonated forms exist in equilibrium. Therefore, it is to be expected that the correlation yields a complicated pattern. Since we currently have data on hand only for four compounds any attempt to draw conclusions from the comparison of their behavior would be speculative at this time.

Correlation of anilines pK_α values in THF with pK_a values in AN gives the following equation: $pK_a(AN) = 5.55 + 0.971pK_\alpha$ (THF); s(intercept) $= 0.04$, s(slope) $= 0.007$, $n = 4$, $r^2 = 1.000$, $S = 0.01$. In THF medium the directly experimentally determined basicity values are the ion-pair basicities denoted as pK_{ip}. The pK_α value is an approximation of the ionic pK_a value (referring to free ions) that has been obtained using the Fuoss equation to take the ion pair formation into account. See refs 10 and 24 for details. It appears that basicity of anilines is almost equally sensitive toward substitution in the aromatic ring in AN and in THF (Figure 2).

Correlation of the basicities of 4-substituted anilines (including the 4-methylaniline from ref 21) with the σ_F and σ_R substituent constants[57] yields the following equation: $pK_a(AN) = pK_a^0 + \rho_F\sigma_F + \rho_R\sigma_R$, where $pK_a^0 = 10.52$; $s(pK_a^0) = 0.19$; $\rho_F = -4.68$; $s(\rho_F) = 0.45$; $\rho_R = -6.50$; $s(\rho_R) = 0.57$; $n = 6$; $S = 0.25$; $r^2 = 0.991$.

Pyridines. Correlation of pK_a values in water with pK_a values in AN gives the following equation: pK_a (AN) $= 6.04 + 1.269$ pK_a (H_2O); s(intercept) $= 0.30$, s(slope) $= 0.048$, $n = 15$, $r^2 = 0.982$, $S = 0.46$. Correlation of pK_α values in THF with pK_a values in AN gives the following equation: pK_a (AN) $= 7.44 + 0.934$ pK_α (THF); s(intercept) $= 0.05$, s(slope) $= 0.007$, $n = 7$, $r^2 = 1.000$, $S = 0.05$. Correlation of gas-phase basicities ($pK_a(GB) = GB{\cdot}2.30/R{\cdot}T = GB/1.364$) with pK_a values in AN gives the following equation: $pK_a(AN) = -82.62 + 0.597$ $pK_a(GB)$; s(intercept) $= 11.71$, s(slope) $= 0.073$, $n = 11$, $r^2 = 0.882$, $S = 1.21$.

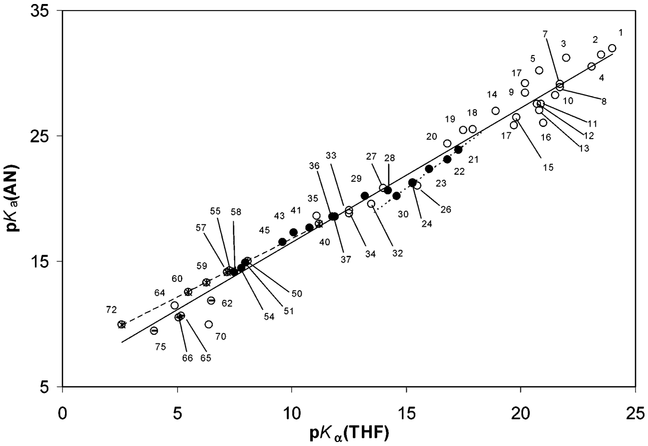

FIGURE 2. Correlation of studied bases basicities in THF and acetonitrile. Solid line corresponds to overall correlation; dotted line corresponds to 4-substituted-PhP1(pyrr)-s; dashed line corresponds to pyridines. Overall correlation: $pK_a(AN) = 5.78 + 1.071pK_\alpha(THF)$; s(intercept) $= 0.32$, s(slope) $= 0.021$, $n = 55$, $r^2 = 0.980$, $S = 0.93$.

Phosphazenes. The Effect of Para Substitution. Correlation of pK_α values in THF with pK_a values in AN of 4-substituted PhP_1(pyrr)-s gives the following equation: pK_a (AN) $= 0.47 + 1.354pK_\alpha$ (THF); s(intercept) $= 1.02$, s(slope) $= 0.064$, $n = 5$, $r^2 = 0.993$, $S = 0.14$. Correlation of pK_α values in THF with pK_a values in AN of the 4-substituted PhP_3(dma)-s gives the following equation: pK_a (AN) $= 1.42 + 1.276$ pK_α (THF); s(intercept) $= 1.22$, s(slope) $= 0.053$, $n = 3$, $r^2 = 0.998$, $S = 0.09$. The slopes of these two correlations differ from overall correlation of substituted PhP_1(pyrr)-s: pK_a (AN) $= 7.45 + 0.929pK_\alpha$ (THF); s(intercept) $= 0.37$, s(slope) $= 0.029$, $n = 15$, $r^2 = 0.987$, $S = 0.36$, which is similar to series of substituted pyridines (0.93) and anilines (0.97) (see above).

Correlation of the basicities of 4-substituted PhP_1(pyrr) phosphazenes (**21**, **22**, **23**, **25**, **30**, **38**) with the σ_F and σ_R constants[57] of the substituents yields the following equation: $pK_a(AN) = pK_a^0 - \rho_F\sigma_F - \rho_R\sigma_R$, where $pK_a^0 = 22.35$; $s(pK_a^0) = 0.31$; $\rho_F = -4.35$; $s(\rho_F) = 0.68$; $\rho_R = -4.48$; $s(\rho_R) = 0.55$; $n = 6$; $S = 0.32$; $r^2 = 0.985$. The sensitivity of the basicity of phosphazenes PhP_1(pyrr) to electronegativity of the substituents (ρ_F) is similar to that of anilines. The sensitivity to resonance effect of the substituents (ρ_R) is significantly lower in the case of PhP_1(pyrr) phosphazenes.

If we follow the change in free ion basicities of PhP_n(dma) ($n = 0...3$, compounds **64**, **24**, **15**, **2**) in those two media we observe following base strengthening effect upon addition of phosphazene groups into a molecule, in AN: 9.82; 5.21; 5.02 pK_a units and in THF: 10.4; 4.5;

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(52) Koppel, I. A.; Koppel, J.; Maria, P.-C.; Gal, J.-F.; Notario, R.; Vlasov, V. M.; Taft, R. W. *Int. J. Mass Spectrom. Ion Processes* **1998**, *175*, 61–69.

(53) Taft, R. W. *Prog. Phys. Org. Chem.***1983**, *14*, 247–350.

(54) (a) Lee, S.-W.; Cox, H.; Goddard, W. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 9201–9205. (b) Summerhays, K. D.; Pollack, S. K.; Taft, R. W.; Hehre, W. *J. Am. Chem. Soc.* **1977**, *99*, 4585–4587. (c) Lau. Y. K.; Nishizawa, A. T.; Brown, R. S.; Kebarle, P. *J. Am. Chem. Soc.* **1981**, *103*, 6291–9295.

(55) Russo, N.; Toscano, M.; Grand, A. Mineva, T. *J. Phys. Chem. A* **2000**, *104*, 4017–4021. (b) Maria, P.-C.; Leito, I.; Gal, J.-F.; Exner, O.; Decouzon, M. *Bull. Soc. Chim. Fr.* **1995**, *132*, 394–401.

(56) (a) Pollack, S. K.; Devlin, J. L.; Summerhays, K. D.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4583–4584. (b) Bagno, A. Terrier, F. *J. Phys. Chem. A* **2001**, *105*, 6537–6542.

(57) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

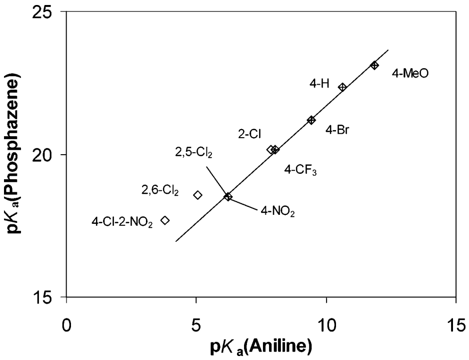

FIGURE 3. Correlation of pK_a values in AN of phenyl-substituted anilines and PhP$_1$(pyrr) phosphazenes. The solid line corresponds to the correlation equation of the para-substituted compounds. The most deviating points belong to the 2,6-Cl$_2$- (**36**) and 4-Cl-2-NO$_2$-substituted (**41**) compounds.

3.7 pK_a units, respectively. The addition of first N=P(dma)$_2$ subunit into the amine **64** molecule is more expressed in THF (ratio 0.94). The addition of second and third N=P(dma)$_2$ subunit into the molecules **24** and **15**, respectively, the basicity is 1.16 and 1.36 times stronger expressed in AN than in THF. Schwesinger[2] reports in the row t-BuP$_n$(dma) (n = 0...5) the following base strengthening effect upon addition of phosphazene N=P(dma)$_2$ subunits into a molecule in AN: approximately 8.5, 6.61, 5.1, 4.1, 2.6 pK_a units, last three being extrapolated from experiments in other solvents. This row is quite similar to ours.

Comparison of pK_a Values of Anilines and Aryliminophosphoranes. It is of interest to compare the basicities of the substituted PhP$_1$(pyrr)-s with corresponding anilines. pK_a values of substituted anilines in AN correlate well with pK_a values of PhP$_1$(pyrr) in AN: pK_a(PhP$_1$(pyrr))$_{AN}$ = 14.61 + 0.706 pK_a(Aniline)$_{AN}$; s(intercept) = 0.38, s(slope) = 0.047, n = 9, r^2 = 0.970, S = 0.35. For only 4-C$_6$H$_4$ substitution the correlation is as follows: pK_a(PhP$_1$(pyrr))$_{AN}$ = 13.46 + 0.824 pK_a(aniline)$_{AN}$; s(intercept) = 0.26, s(slope) = 0.027, n = 5, r^2 = 0.997, S = 0.12. As seen, the basicity of PhP$_1$(pyrr) is less sensitive toward substitution in the aromatic ring than basicity of anilines. Lower sensitivity can be due to the contribution of the ylenic structure in the substituted PhP$_1$(pyrr) series[6] and delocalization of the positive charge of the protonated form into the large phosphorane moiety (Figure 3).

All these above given correlations can help one to predict the basicities of various types of bases when transforming these from one medium to another.

Comparison with Theoretical Calculations. Recently, progress has been made in theoretical computing of condensed phase pK_a values.[15,62] In particular, important contributions on linking theoretically calculated values to pK_a values in AN have been published by the Maksić group[15] who have recently shown that pK_a(AN) values of some selection of strong organic bases in AN could be described by the density functional theory (B3LYP/6-311+G**//HF/6-31G* level) using isodensity polarization continuum model for the calculation of solvent−solute interactions and proton affinities PA(AN) of those bases in AN solution. The theoretical pK_a(AN) values and PA(AN), are available[15] for a few compounds **8**, **14**, **16**, **17**, **18**, **23**, **24**, **27**, **35**, and **65** from Table 1 covering the basicity range from 10.6 to 28.9 pK_a(AN) units. There is a good correlation between experimental pK_a(AN) values from this work and the pK_a(AN)$_{calc}$ values for the above-mentioned selection of compounds: pK_a(AN) = −0.67 + 1.021 pK_a(AN)$_{calc}$; s(intercept) = 0.77, s(slope) = 0.033, n = 10, r^2 = 0.992, S = 0.51. Although the correlation has in general unity slope the approach used in this theoretical calculation model introduces in some cases (e.g. ΔpK_a of compounds **23** and **24** in theory and experiment, pK_a of **35** in theory and experiment) deviations that by far exceed the experimental deviations.

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Supporting Information Available: Description and purification procedures of the compounds, the ^{13}C NMR spectra of a new compound (**38**), and description of the experimental setup. This material is available free of charge via the Internet at http://pubs.acs.org.

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(58) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Phys. Chem.* **1968**, *72*, 2270−2272.

(59) Schwesinger, R.; Schlemper, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1167−1169.

(60) Bernasconi, C. M.; Leyes, A. E.; Ragains, M. L.; Shi, Y.; Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8632−8639.

(61) Barrón, D.; Butí, S.; Ruiz, M.; Barbosa, J. *Polyhedron* **1999**, *18*, 3281−3288.

(62) Almerindo, G. I.; Tondo, T. W.; Pliego, J. R., Jr. *J. Phys. Chem.* **2004**, *108*, 166−171.