Experimental Gas-Phase Basicity Scale of Superbasic Phosphazenes

Ivari Kaljurand,[†] Ilmar A. Koppel,[†] Agnes Kütt,[†] Eva-Ingrid Rõõm,[†] Toomas Rodima,[†] Ivar Koppel,[†] Masaaki Mishima,[‡] and Ivo Leito*,[†]

Department of Chemistry, University of Tartu, Jakobi 2 str, 51014 Tartu, Estonia, and Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received: September 21, 2006; In Final Form: December 2, 2006

Seventeen superbasic phosphazenes and two Verkade's bases were used to supplement and extend the experimental gas-phase basicity scale in the superbasic region. For 19 strong bases the gas-phase basicity values (GB) were determined for the first time. Among them are such well-known bases as BEMP (1071.2 kJ/mol), Verkade's Me-substituted base (1083.8 kJ/mol), $Et-N=P(NMe_2)_2-N=P(NMe_2)_3$ ($Et-P_2$ phosphazene, 1106.9 kJ/mol), and $t\text{-}Bu-N=P(NMe_2)_3$ ($t\text{-}Bu-P_1$ phosphazene, 1058.0 kJ/mol). For the first time experimental GB values were determined for P_2 phosphazenes. Together with our previous results self-consistent experimental gas-phase basicity scale between 1020 and 1107 kJ/mol is now established. This way an important region of the gas-phase basicity scale, which was earlier dominated by metal hydroxide bases, is now covered also with organic bases making it more accessible for further studies. The GB values for several superbases were calculated using density functional theory at the B3LYP/6-311+G** level. For the phosphazene family the standard deviation of the correlation between the experimental and theoretical values was 6.5 kJ/mol.

Introduction

Superbasic phosphazene bases have been under extensive study during recent years. They are used in synthesis;[1−3] aryl phosphazenes have proved to be very suitable for building the superbasic region of self-consistent Brønsted basicity scales in acetonitrile[4] (AN) and THF.[5−8] The possibility to predictably fine-tune the basicities of aryl phosphazenes by insertion of various substituents into the phenyl ring, by varying the structure of the aliphatic periphery or using higher phosphazene homologues, makes this family very flexible for designing molecules with predictable basicity. Also the gas-phase basicity (GB) values for some phosphazene bases have been calculated[7−9] and experimentally determined.[6,10] In our previous work[6] a limited selection of P_1 phosphazenes was studied. The obtained results were in part surprising as they implied that the GB values of aryl substituted phosphazenes, compared to the basicities in THF, were rather insensitive toward the substituent in the aromatic nucleus.

To further study this surprising result, a wider selection of aryl substituted P_1 phosphazenes was taken into the study described in this report. Also, several attempts to experimentally determine the basicity change when going from P_1 phosphazenes to P_2 phosphazenes for two homological series were made. For the sake of comparison two Verkade's bases[12] (see Chart 1 for structures and designations) and three bicyclic guanidine bases (MTBD, ETBD, ITBD) were also included in the continuous basicity ladder. MTBD was used as the anchoring point for the measurements reported in this work.

It has been suggested more than a decade ago that phosphazene superbases could be one of the most promising families of compounds for extending the continuous gas-phase basicity

scale of organic compounds into the domain of very strong bases.[11] However, the practical success in realization of this promise has been very limited to date. To the best of our knowledge there have been only two works reporting experimental gas-phase basicity data for phosphazene bases,[6,10] both reporting data only for a very narrow selection of compounds. This situation is caused by the serious experimental complications that arise when measuring the gas-phase basicities of phosphazene bases. The foremost among these is the very low volatility of most of these compounds making it very difficult to achieve and maintain suitable and constant vapor pressure in the mass spectrometer. Also, it is necessary to have on hand a range of bases with gradually changing basicities in order to be able to build a continuous "ladder".

In this work we have succeeded to overcome both of these complications (see the Supporting Information for experimental details), and we present a continuous phosphazene-based gas-phase basicity ladder with the span of ca. 87 kJ/mol from which around 40 kJ/mol is an extension of the so far existing continuous gas-phase basicity scale of organic bases.

Experimental Section

Chemicals. Compounds **1**, **3**, **7**, **9**, **12**, **13**, **18**, and **23** were of commercial origin and were used in ICR experiments without additional purification. Synthesis, purification, and identification of **2**, **4**, **5**, **8**, **10**, **11**, **14−17**, **19**, **20**, **21**, and **24−30** has been described in previous works.[5−7,13] HCl salt of **6** was synthesized as described in ref 14. The salt was converted into tetrafluoroborate salt by treatment with $NaBF_4$ in water. The free base was liberated from the HBF_4 salt by means of MeOK in MeOH. ETBD (**22**) was a kind donation from Prof. Reinhard Schwesinger (University of Freiburg).

Measurements of Gas-Phase Basicity (GB$_{exp}$). The instrumentation, general experimental setup, and conditions have been previously described.[6] Detailed experimental conditions for introducing low-volatile bases into the ICR cell are given in

* Corresponding author. Phone: +372 7 375 259. Fax: +372 7 375 264. E-mail: ivo.leito@ut.ee.
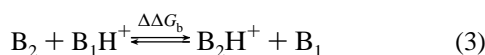† University of Tartu.
‡ Kyushu University.

CHART 1:
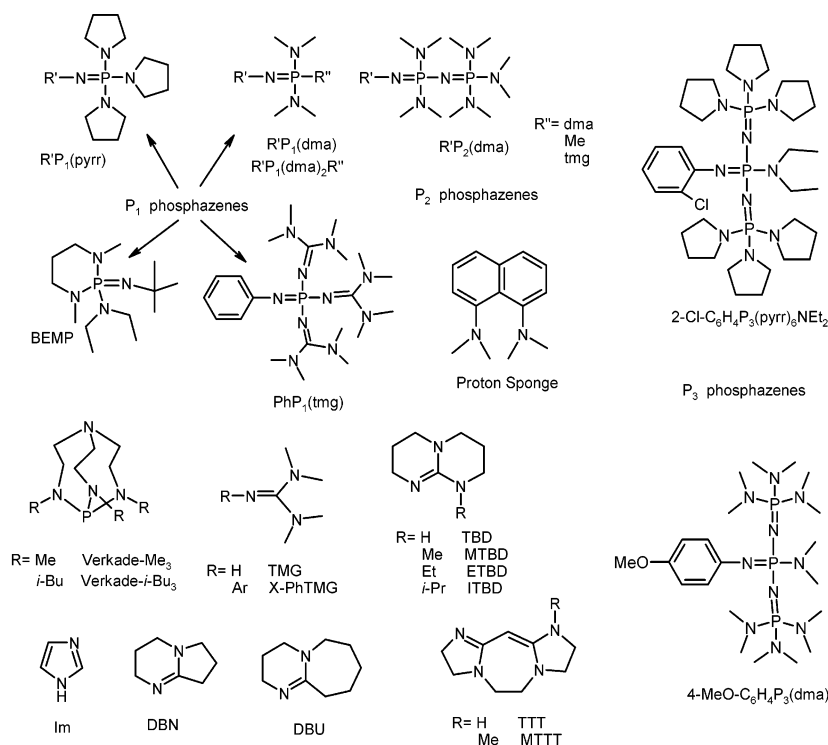
the Supporting Information. Gas-phase basicity (GB) and proton affinity (PA) refer to the following equilibrium:

$$B + H^+ \underset{}{\overset{\Delta G_b \Delta H_b}{\rightleftharpoons}} BH^+ \qquad (1)$$

GB and PA are defined as follows:

$$GB = -\Delta G_b \quad PA = -\Delta H_b \qquad (2)$$

The directly measured quantity is the relative basicity of two bases $\Delta\Delta G_b$:

$$B_2 + B_1 H^+ \overset{\Delta\Delta G_b}{\rightleftharpoons} B_2 H^+ + B_1 \qquad (3)$$

where

$$\Delta\Delta G_b = \Delta G_b(B_2) - \Delta G_b(B_1) = -RT \ln K \qquad (4)$$

$$K = \frac{p(B_1) \cdot I(B_2 H^+)}{p(B_2) \cdot I(B_1 H^+)} \qquad (5)$$

The p and I values are the partial pressures and ion intensities of the respective species.

Computations of Gas-Phase Basicity. The quantum-chemical computations reported in this work were carried out using the Gaussian 2003 series of programs.[15] Density functional theory (DFT) calculations were performed using the B3LYP hybrid functional. Full geometry optimizations and vibrational analyses were performed using the 6-311+G** basis set. This approach has been demonstrated by some of us to describe with reasonable accuracy the gas-phase basicities[8,16] of a wide variety of relatively simple molecules. All stationary points were found to be true minima ($N_{imag} = 0$). Unscaled B3LYP/6-311+G** frequencies were used to calculate the GB and PA values of the neutral bases taking into account the zero point frequencies,

finite temperature 0−298 K correction, the pressure-volume work term, and the entropy term as appropriate.

Results

Gas-Phase Basicity Measurements. In addition to previously[6] determined GB values for phosphazenes, in the present work 39 $\Delta\Delta G_b$ measurements between 25 superbases were carried out. Together with results from ref 6 these form the extension of the so far existing[10,17] experimental self-consistent gas-phase basicity scale toward the region of higher basicity. MTBD was chosen as the anchor compound for the present scale as its published GB value (GB = 1030.2 kJ/mol)[17] has been observed by measuring it against two reference bases, while the GB values of ITBD and ETBD, which would otherwise also be suitable as anchors, have been obtained only against one compound. The results are presented in Table 1.

Gas-Phase Basicity Calculations. The results of calculation of the basicities of the phosphazene superbases described in this work are summarized in Tables 1 and S3 in the Supporting Information. Detailed results of the calculations and the Cartesian coordinates of the calculated species are available in the Supporting Information.

Discussion

Extension of the Experimental Gas-Phase Basicity Scale. For several decades the experimental gas-phase basicity scale in the region above MTBD (GB = 1030.2 kJ/mol) has been based mainly on alkali and alkaline earth metal oxides and hydroxides. These compounds are difficult to handle in gas-phase basicity measurements, making it difficult to use them as reference bases for further measurements. According to the current NIST Webbook and ref 17, MTBD is the most basic organic compound having GB value obtained by direct comparison against several reference bases. There are some other bases $(CH_3)_2NC(CH_3)=N-(CH_2)_3N(CH_3)_2$, ETBD, ITBD, TTT, and MTTT that are more basic, but these have been measured

TABLE 1: Experimental and Calculated Gas-Phase Basicities of the Studied Bases

No	Base	Directly measured $\Delta\Delta G_b{}^a$	$GB_{exp}{}^b$	$GB_{calc}{}^c$
1	EtP$_2$(dma)		1106.9	1112.5
2	PhP$_2$(dma)		1094.9	1084.5 [f]
3	Verkade-iBu$_3$		1091.2	
4	2-Cl-C$_6$H$_4$P$_2$(dma)		1089.8	1082.4
5	EtP$_1$(pyrr)		1085.9	1078.6
6	Verkade-Me$_3$		1083.8	1066.9
7	t-BuP$_1$(pyrr)		1082.5	1080.3
8	4-Me$_2$N-C$_6$H$_4$P$_1$(pyrr)		1077.3	
9	BEMP		1071.2	1069.4
10	HP$_1$(pyrr)		1067.7	1066.9 [f]
11	4-MeO-C$_6$H$_4$P$_1$(pyrr)		1066.6	
12	t-OctP$_1$(dma)		1063.7	
13	t-BuP$_1$(dma)		1058.0	1054.8
14	MeP$_1$(dma)		1054.0	1055.6 [g]
15	PhP$_1$(pyrr)		1053.0	1049.8
16	1-NaphtP$_1$(pyrr)		1050.1	
17	2-Cl-C$_6$H$_4$P$_1$(pyrr)		1049.2	
18	HP$_1$(dma)		1044.6	1044.3 [g]
19	4-Br-C$_6$H$_4$P$_1$(pyrr)		1043.1	
20	2,5-Cl$_2$-C$_6$H$_3$P$_1$(pyrr)		1038.8	1021.7
21	ITBD		1037.2	1042.2
22	ETBD		1035.7	1026.3
23	MTBD [d]		1030.2 [d]	1037.6
24	PhP$_1$(dma)		1029.9	1026.3 [f]
25	2-NO$_2$-5-Cl-C$_6$H$_3$P$_1$(pyrr)		1028.5	
26	4-CF$_3$-C$_6$H$_4$P$_1$(pyrr)		1026.8	
27	2,6-Cl$_2$-C$_6$H$_3$P$_1$(pyrr)		1026.3	1035.5
28	2-NO$_2$-4-Cl-C$_6$H$_3$P$_1$(pyrr)		1024.9	1030.9
29	2-Cl-C$_6$H$_4$P$_1$(dma)		1019.9	1017.5
30	PhP$_1$(dma)$_2$Me		1019.7	1015.5

Directly measured $\Delta\Delta G_b$ ladder values (kJ/mol): 10.5, 3.3, 23.8, 2.5, 4.6, 23.0, 7.9, 11.5, 8.4, 7.4, 3.3, 2.5, 10.5, 2.1, 9.2, 16.3, 6.8, 2.2, 14.6, 2.5, 7.5, 1.5, 4.3, 7.5 [e], 5.7, 3.8 [e], 4.2 [e], 0.8 [e], 9.2 [e], 30.5 [e], 5.0 [e], 13.8 [e], 0.7, 12.6 [e], 20.1 [e], 9.2 [e], 11.7 [e], 1.7 [e], 5.1, 1.5, 8.4 [e], 5.8, 0.4, 7.1, 1.4, 3.1, 3.8, 4.9, 10.5, 6.6, 7.1, 5.1, 0.4.

^{a} Directly measured experimental $\Delta\Delta G_b$ (kJ/mol) values obtained from FT−ICR measurements. ^{b} Experimental absolute GB (kJ/mol) values for bases. 1 kcal/mol = 4.184 kJ/mol. ^{c} Results of basicity calculations at DFT B3LYP/6-311+G** level (kJ/mol), this work if not noted otherwise. ^{d} Anchor of the scale, GB value taken from ref 17. ^{e} Reference 6. ^{f} Reference 7. ^{g} Reference 8.

reliably only against one reference compound or their gas-phase basicity values are approximate. The results of this work have extended the gas-phase basicity scale of organic compounds to GB = 1107 kJ/mol. The following compounds—EtP$_2$(dma), HP$_1$-(dma), t-BuP$_1$(dma), t-OctP$_1$(dma), t-BuP$_1$(pyrr), BEMP, MTBD and also both studied Verkade's bases (trimethyl- and triisobutyl-substituted)—are commercially available and thus provide convenient references for other investigators for further basicity studies in this region. Also, small amounts of the noncommercial bases used in this work are available from the authors on request.

Experimental GB values for two homological series of phosphazenes—for the pair **24** and **2** and for pair **29** and **4** are now available. The base-strengthening effects in the homological rows, when going from arylsubstituted P$_1$ to P$_2$ phosphazenes, are 65.1 and 69.9 kJ/mol, respectively. This gives a direct experimental support for the previous findings of theoretical works[7,8] to use a homological series of phosphazenes to further extend the basicity scale in the gas phase.

The recently introduced guanidinophosphazenes[7] (containing different substituted guanidino fragments besides amino frag-ments) are a very promising series of bases for expanding the existing experimental basicity scale toward higher basicity range. For example, the GB value of tris-*N′,N′,N″,N″*-tetramethylguanidino derivative of phenyl P$_1$ phosphazene—PhP$_1$(tmg)—is calculated to be 1146.4 kJ/mol (see Table S3 in the Supporting Information). In THF solution, for the stepwise substitution of dma groups with tmg groups in the PhP$_1$(dma) (pK_α(THF)=15.3) the following basicity order was observed: 18.4, 21.5, and 24.3 pK_α(THF) units.[7] These values lead us to conclusion that using these three parent compounds and additionally introducing various substituents into the phenyl ring one can cover the basicity range up to 1146 kJ/mol with members of these three families. This prediction is also supported by the basicity measurements in THF and acetonitrile medium (see Table 2). For example, the PhP$_1$(tmg) phosphazene successfully competes in basicity with P$_3$ phosphazenes.

Correlation of GB$_{exp}$ with GB$_{calc}$. It is of great interest to compare the experimentally measured and calculated at the DFT B3LYP/6-311+G** level GB values of the compounds studied in the present work. The overall correlation of available data

TABLE 2: Results of UV−Vis Spectrophotometric pK_{ip}(THF), pK_α(THF), and pK_a(AN) Measurements

		In THF[a]			
compound (B$_1$)	reference (B$_2$)	pK_{ip}(HB$_2^+$A$^-$)	ΔpK_{ip}	pK_{ip}	assigned pK_α value
BEMP	PhP$_2$(dma)	19.43	0.17	19.3	19.0
	PhP$_1$(dma)$_2$tmg	18.13	−1.15	19.3	
t-OctP$_1$(dma)	PhP$_2$(dma)	19.43	1.0	18.4	18.5
	PhP$_1$(dma)$_2$tmg	18.13	−0.4	18.5	

		In AN[b]			
compound (B$_1$)	reference (B$_2$)	pK_a(HB$_2^+$)	ΔpK_a	pK_a(HB$_1^+$)	assigned pK_a(HB$_1^+$) value
2-Cl−C$_6$H$_4$P$_2$(dma)	4-MeO−C$_6$H$_4$P$_1$(pyrr)	23.12	−1.11	24.23	24.25
	PhP$_1$(dma)$_2$tmg		0.46		
PhP$_1$(dma)$_2$tmg	PhP$_2$(dma)	26.46	1.62	24.84	24.72
PhP$_1$(tmg)	4-MeO−C$_6$H$_4$P$_3$(dma)	31.99	0.58	31.41	31.4
	2-Cl−C$_6$H$_4$P$_3$(pyrr)$_6$NEt$_2$	31.19	0.15	31.34	

[a] In THF the equilibria are defined by eqs 2 and 3 in the Supporting Information. [b] In AN eq 5 in the Supporting Information is used for ΔpK_a calculation.

TABLE 3: Correlation of GB$_{exp}$ and GB$_{calc}$ Values Calculated at the DFT B3LYP/6-311+G Level of Organic Bases above 753 kJ/mol[a]**

	a	s(a)	b	s(b)	S	R^2	n
all bases	1.01	0.01	−12.6	11.1	7.9	0.992	63
all bases of present work	1.01	0.06	−5.2	66.4	7.4	0.931	21
phosphazenes of present work	0.99	0.06	15.0	61.1	6.5	0.951	17
all non-phosphazenes bases	0.99	0.02	7.7	14.4	7.9	0.988	46

[a] The following notations are used: a − slope, s(a) − standard deviation of slope, b − intercept, s(b) − standard deviation of intercept, S − overall standard deviation of the correlation, R^2 − squared correlation coefficient, and n − number of data points in the correlation.

above GB = 753 kJ/mol presented in Tables 1 and S3 in the Supporting Information gives the following equation: GB$_{exp}$ = 1.01 GB$_{calc}$ − 12.6, the standard deviations of the slope and intercept are 0.01 and 11.1, respectively, and R^2 = 0.992, n = 63, and S = 7.9 kJ/mol. The correlation containing only bases measured in this work is similar: GB$_{exp}$ = 1.01 GB$_{calc}$ − 5.2, the standard deviations of the slope and intercept are 0.06 and 66.4, respectively, and R^2 = 0.931, n = 21, and S = 7.4 kJ/mol. The quality (in terms of the S value, i.e., the average spread of points around the correlation line) of the two correlations is similar in spite of difficulties arising in both experimental measurements (poor volatility and very long pressure stabilization period of aryl-phosphazene bases in ICR experiments) and calculations (high demand of calculation power, danger to stop at local energy minima, etc.). These two correlations and two other correlation series given in Table 3 are all in agreement with previous findings[16] that GB values for neutral bases calculated at the DFT B3LYP/6-311+G** level are of comparable quality with experimental measurements. The standard deviation (7.9 kJ/mol) of overall correlation observed in this work for the GB range 753−1107 kJ/mol is similar to the standard deviation (7.5 kJ/mol) observed in the previous work[16] for the GB range from 146 to 1163 kJ/mol of various bases.

Out of the bases measured in this work the most deviating from the correlation are bases **6** (−17.4 kJ/mol) and **20** (−18.0 kJ/mol) (correlation given in the second line of Table 3). According to the correlation parameters these deviations are random and can be explained by statistics. If we assume linearity and normal distribution of the sample population over the GB range, then approximately 68% of the GB$_{exp}$ values should fall within the range of GB$_{calc}$ ± 1S, approximately 95% of the GB$_{exp}$ values should fall within the range of GB$_{calc}$ ± 2S (i.e.,

±14.8 kJ/mol), and approximately 99.7% of the GB$_{exp}$ values should fall within the range of GB$_{calc}$ ± 3S (i.e., ±22.2 kJ/mol). With our data these proportions are the following: 67% of the data fall within ± 1S limits, 90% of the data fall within ± 2S, and all values fall within the ± 3S limits. Given the low (in terms of statistics) number of points (21) the behavior of the outliers can well be considered statistical, and it is not justified to try to link the deviations to some structural effects in the bases on the basis of the present data.

Correlation of GB$_{exp}$ Values of Various Bases. The available[17] GB values for ring-substituted anilines and ring-substituted N,N-dimethylanilines (DMA-s) which have the same substituents as PhP$_1$(pyrr) phosphazenes are presented in Table S3 in Supporting Information. Also GB$_{exp}$ values for the same substitution series of N,N-dimethyl-N'-phenylformamidines (Ph-DMFA-s) have been published:[18] 990.8, 974.5, 959.8, and 936.0 kJ/mol for 4-Me$_2$N, 4-MeO, 4-H, and 4-CF$_3$, respectively. Figure 2 presents the correlations of the GB values of ring-substituted PhP$_1$(pyrr)s and respective anilines, DMA-s and PhDMFA-s. The correlation between PhP$_1$(pyrr) phosphazenes and anilines is excellent: GB$_{exp}$(PhP$_1$(pyrr)) = 0.703 GB$_{exp}$(aniline) + 455.9, the standard deviations of the slope and intercept are 0.020 and 16.9, respectively, and R^2 = 0.999, n = 3, and S = 0.8 kJ/mol. It was also observed in AN solution, that pK_a values of 4-X-PhP$_1$(pyrr) phosphazenes are in comparison with 4-X-anilines less[4] (0.82 times) sensitive toward substituent in phenyl ring. The 4-Me$_2$N-aniline protonates at dimethylamino group; therefore, this compound is not a true member of the family, and its experimental GB value was left aside from the correlation. With DMA-s the correlation is slightly inferior: GB$_{exp}$(PhP$_1$(pyrr)) = 0.862 GB$_{exp}$(DMA) + 270.8, the standard deviations of the slope and intercept are 0.051 and 45.9, respectively, and R^2 = 0.997, n = 3, and S = 1.7 kJ/mol. The correlation with PhDMFA-s is as follows: GB$_{exp}$(PhP$_1$(pyrr)) = 0.932 GB$_{exp}$(PhDMFA) + 156.4, the standard deviations of the slope and intercept are 0.075 and 72.7, respectively, and R^2 = 0.987, n = 3, and S = 3.0 kJ/mol.

Correlations of GB$_{exp}$ with Solution Basicities. Additional discussion of the relationship of gas-phase and solvent basicities can be found in the Supporting Information. The solvent influence on compounds basicity is obtained by correlating basicity values in the gas phase and solvent. The correlation equation has the following form

$$GB(kJ/mol) = a\ pK(X) + b \qquad (6)$$

Superbasic Phosphazenes
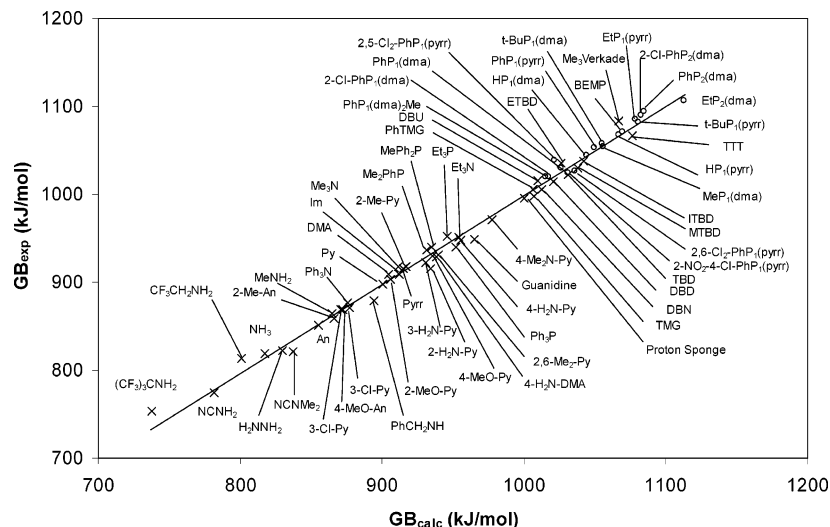
J. Phys. Chem. A, Vol. 111, No. 7, 2007 **1249**

Figure 1. Comparison of the calculated gas-phase basicity values (GB$_{calc}$) and experimental gas-phase basicity values (GB$_{exp}$). ○ - denotes phosphazenes, × - non-phosphazene bases, the solid line corresponds to overall correlation.
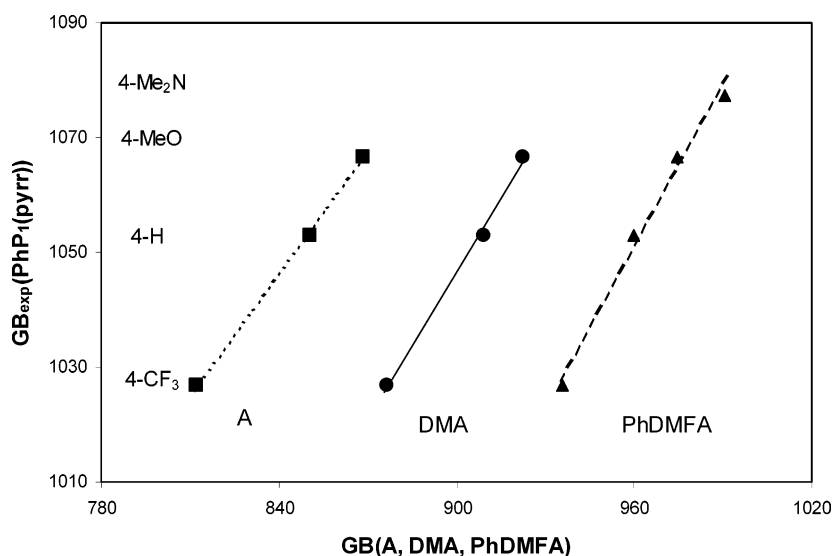

Figure 2. Correlations of experimental gas-phase basicity values (GB) of *para* substituted PhP$_1$(pyrr) phosphazenes with the respective values of anilines (A) (■), DMA-s (●), and PhDMFA-s (▲).

where pK(X) denotes basicity value in a solvent X, and a and b are the slope and intercept, respectively.

Conclusions

For several decades the experimental gas-phase basicity scale in the region above MTBD (GB = 1030.2 kJ/mol) has been based mainly on alkali and alkaline earth metal oxides and hydroxides. The results of this work have extended the continuous gas-phase basicity scale of organic compounds further to GB = 1106.9 kJ/mol. The following compounds—EtP$_2$(dma), HP$_1$(dma), t-BuP$_1$(dma), t-OctP$_1$(dma), t-BuP$_1$(pyrr), BEMP, MTBD, and also both used Verkade's bases—are commercially available and thus provide convenient references for other investigators for further basicity studies in this region. Also, small amounts of the noncommercial bases used in this work are available from the authors on request.

Work is in progress in the laboratories of the authors to further extend the gas-phase basicity scale using stronger phosphazene bases (P$_2$, P$_3$, and P$_4$ phosphazenes, guanidinophosphazenes,[7] etc).

Supporting Information Available: Details of the experimental gas-phase and solution basicity measurements and extended version of Table 1 (Table S3) containing detailed calculation and experimental data, correlations and discussion of gas-phase and solution basicities, and geometry data of the calculated molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(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) (a) For a comprehensive review on application of phosphazene bases, see: *Strong and Hindered Bases in Organic Synthesis*; Vol. 3, No. 1. www.sigmaaldrich.com/Area_of_Interest/Chemistry/Chemical_Synthesis/Key_Resources/ChemFiles/Vol_3_No_1.html (accessed January 2007). (b) Bensa, D.; Constantieux, T.; Rodriguez, J. *Synthesis* **2004**, 923−927.

(4) Kaljurand, I.; Kütt, A.; Soováli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019−1028.

(5) Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2002**, *67*, 1873−1881.

(6) Kaljurand, I.; Rodima, T.; Pihl, A.; Mäemets, V.; Leito, I. A.; Mishima, M. *J. Org. Chem.* **2003**, *68*, 9988−9993.

(7) Kolomeitsev, A. A.; Koppel, I. A.; Rodima, T.; Barten, J.; Lork, E.; Röschenthaler, G.-V.; Kaljurand, I.; Kütt, A.; Koppel, I.; Mäemets, V.; Leito. I. *J. Am. Chem. Soc.* **2005**, *127*, 17656−17666.

(8) Koppel, I. A.; Schwesinger, R; Breuer, T.; Burk, P.; Herodes, K.; Koppel, I.; Leito, I.; Mishima, M. *J. Phys. Chem. A* **2001**, *105*, 9575−9586.

(9) Kovačević, B.; Barić, C.; Maksić, Z. B. *New J. Chem.* **2004**, *28*, 284−286.

(10) Raczyńska, E. D.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Woźniak, K.; Kurg, R.; Carins, S. N. *Trends Org. Chem.* **1998**, *7*, 95−103.

(11) Raczyńska, E. D.; Maria, P. C.; Gal, J. F.; Decouzon, M. *J. Phys. Org. Chem.* **1994**, *7*, 725−733.

(12) (a) Kárpáti, T.; Vezprémi, T.; Thirupathi, N.; Liu, X.; Wang, Zh.; Ellern, A.; Nyulászi, L.; Verkade, J. G. *J. Am. Chem. Soc.* **2006**, *128*, 1500−1512. (b) Galasso, V. *J. Phys. Chem. A* **2004**, *108*, 4497−4504. (c) Nyulászi, L.; Veszprémi, T.; D'Sa, B. A.; Verkade, J. *Inorg. Chem.* **1996**, *35*, 6102−6107. (d) Windus, T. L.; Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 11449−11455.

(13) Rodima, T.; Mäemets, V.; Koppel, I. *J. Chem. Soc. Perkin Trans. 1* **2000**, 2637−2644.

(14) Schmidt, H.; Lensink, C.; Xi, S. K.; Verkade, J. G. *Z. Anorg. Allg. Chem.* **1989**, *578*, 75−80.

(15) *Gaussian 03*, *Revision C.02*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Wallingford, CT, 2004.

(16) Burk, P.; Koppel, I. A.; Koppel, I.; Leito, I. Travnikova, O. *Chem. Phys. Lett.* **2000**, *323*, 482−489.

(17) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 3, 413−656. Most of this GB data is also available at NIST Chemistry WebBook, NIST Standard Reference Database Number 69. http://webbook.nist.gov/chemistry/ (accessed January 2007).

(18) Raczyńska, E. D.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Taft, R. W.; Anvia, F. *J. Org. Chem.* **2000**, *65*, 4635−4640.