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ACID-BASE EQUILIBRIA IN NONPOLAR MEDIA

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LIST OF ORIGINAL PUBLICATIONS

This thesis consists of three articles listed below and a review. The articles are referred in the text by Roman numerals I–III. The review summarizes and supplements the articles.

I. Acid-Base Equilibria in Nonpolar Media. 3. Expanding the Spectrophotometric Acidity Scale in Heptane. Rõõm, E.-I.; Kaljurand, I.; Leito, I.; Rodima, T.; Koppel, I. A.; Vlasov, V. M. *J. Org. Chem.* **2003**, *68*, 7795–7799.

II. Experimental Gas-Phase Basicity Scale of Superbasic Phosphazenes. Kaljurand, I.; Koppel, I. A.; Kütt, A.; Rõõm, E.-I.; Rodima, T.; Koppel, I.; Mishima, M.; Leito, I. *J. Phys. Chem. A* **2007**, *111*, 1245–1250.

III. Brønsted Basicities of Diamines in the Gas Phase, Acetonitrile and Tetrahydrofuran. Rõõm, E.-I.; Kütt, A.; Kaljurand, I.; Koppel, I.; Leito, I.; Koppel, I. A.; Mishima, M.; Goto, K.; Miyahara, Y. *Chem. Eur. J.* **2007**, *accepted*.

Author's contribution

Paper I: The main contributor to the work. Performed most of the calculations and all experimental work.
Paper II: Helped to prepare the manuscript. Performed some experiments.
Paper III: One of two main contributors to writing the text. Performed about half of the experimental work and calculations.

ABBREVIATIONS

A	absorbance
AH	acid
AN	acetonitrile
AN	acceptor number
AU	absorbance unit
B	base
CIP	contact ion-pair
D	dielectric constant, known also as the relative permittivity (ε_r)
DA	diamine
dma	N,N-dimethylamino
DMSO	dimethylsulfoxide
DN	donor number (kcal·mol^{-1})
ε_x^{λ}	molar absorbance coefficient at given wavelength
$\varepsilon_{0x}^{\lambda}$	normalized absorbance coefficient at given wavelength
eq	equation
EPA	electron pair acceptor
EPD	electron pair donor
ΔG	standard molar Gibbs energy change (kcal·mol^{-1})
$\Delta\Delta G_b$	relative gas-phase basicity (kcal·mol^{-1})
$\Delta pK_{a/\alpha/ip}$	relative acidity
GB	gas-phase basicity
HB	hydrogen bond
HBA	hydrogen bond acceptor
HBD	hydrogen bond donor
HC	hydrocarbon
I	relative ion intensity
K	equilibrium constant
K_a	acid dissociation constant
K_α	an estimate of ΔpK_a in case of ion pair acidities or basicities
K_{auto}	autoprotolysis constant
K_{ip}	ion pair dissociation constant
λ	wavelength (nm)
MA	monoamine
n	number of points (in statistical analysis)
n_m	number of measurements (in statistical analysis)
n_c	number of ΔpK_a-s determined (in statistical analysis)
NMR	nuclear magnetic resonance
p	partial pressure
PA	proton affinity (kcal·mol^{-1})

p*K*	the negative logarithm of equilibrium constant
pyrr	N-pyrrolidino
R	gas constant (R = 8.314 J·K^{-1}·mol^{-1}= 1.987 cal·K^{-1}·mol^{-1})
R'P$_n$(R")	phosphazene (iminophosphorane)
s	standard deviation in statistical analysis
S	solution
SSIP	solvent-separated ion-pair
T	absolute temperature (K)
THF	tetrahydrofuran
UV	ultraviolet
Vis	visible

1 INTRODUCTION

Investigation of acid-base equilibria in different media has tremendous importance as the basic physicochemical information. Obtained values of acidity and basicity are widely used in all areas of chemistry, biology, medicine and material science, in both research and industrial field.[1–9] The influence of different media on acidity or basicity of compound depends on a number of solvent properties as well as on the investigated compound itself.[10,11] These properties could be predicted in some extent with several methods (quantum-chemical calculations, equations of Koppel-Palm or Kamlet-Taft, etc).[10,11] Nevertheless, at the current level of development of computational methods experiments still have a huge importance, as even the best prediction methods cannot consider the full complexity of physicochemical effects involved.

The investigation of acid-base properties has started already at the end of the 19th century. Building of self-consistent scales in different media has also been the subject of investigation for quite some time. The first and still most important investigation medium is, of course, water.[12,13] Thousands of compounds have been investigated in water, but water has serious limitations as a solvent for acid-base studies. The most important of these are the high solvating power of water that significantly modifies the acid-base properties of molecules and the quite strong acidic and basic properties of water, which hinder acidity and basicity studies of strong acids and bases, respectively.

Besides water, acid-base equilibria in solvents that are known as good environments for synthesis or electrochemical processes in research and industry, has been investigated quite extensively. The availability of data is quite good in tetrahydrofuran[14–21], acetonitrile[14,22–25] and dimethylsulphoxide[26,27]. Still, the building of acidity and basicity scales in those solvents is an ongoing process. In nonpolar solvents the amount of available data is low but still some investigations have been made.[28–31] Up to now, very little attention have paid to supercritical fluids and ionic liquids — media that are expected to have some very interesting properties for investigations of acid-base properties.

The universal "reference medium" for studies of acid-base properties is the gas phase where intrinsic properties of molecules can be studied. Currently the acidity scale[6,32] with the span 284.1 to 411.7 kcal·mol^{-1} and basicity scale[33] with the span 82.8 to 339.7 kcal·mol^{-1} exist in the gas phase. In the gas phase the theoretical calculation methods are more successful than in any of the condensed media and in the case of small molecules the accuracy of theoretical results can rival the accuracy of experiment.

The goal of this study was to expand the existing acidity scale in heptane and basicity scale in the gas phase, to investigate the family of compounds — α,ω-alkanediamines — in different media, to supplement the existing basicity scales in tetrahydrofuran and acetonitrile with new compounds, and to compare the acidity-basicity data in different solvents and in the gas phase.

2 CONCEPTS AND GENERAL ASPECTS

2.1 Experimental Determination of Gas-Phase Basicities

2.1.1 Brønsted Acid-Base Equilibria in the Gas Phase

Gas-phase basicity (*GB*) and proton affinity (*PA*) of a base B refer to the following equilibrium:

$$B + H^+ \xrightleftharpoons{\Delta G_b, \Delta H_b} BH^+ \qquad (1)$$

GB and *PA* are defined as Gibbs' free energy and enthalpy of 1 reaction respectively:

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

The directly measured quantity is the relative basicity $\Delta\Delta G_b$ of two bases B_1 and B_2:

$$B_2 + B_1H^+ \xrightleftharpoons{\Delta\Delta G_b} B_2H^+ + B_1 \qquad (3)$$

where:

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

$$K = \frac{p(B_1) \cdot I(B_2H^+)}{p(B_2) \cdot I(B_1H^+)} \qquad (5)$$

The *p* values are the partial pressures and *I* values are relative ion intensities of the respective species in the mass spectra.

2.1.2 Experimental Methods of *GB* Determination in the Gas Phase

Acid-base equilibria in the gas phase are widely investigated with the ion cyclotron resonance mass spectrometric (ICR-MS) method. ICR-MS has several advantages for this kind of investigations such as:

(1) The ICR cell works as a reaction cell, where the time between initiating the reaction and detection of reaction products is easily variable, so that the course of the reaction can be followed. In addition, the ions can be manipulated (ejected, excited) for different special purposes.
(2) The method permits to follow multiple reactions that occur in parallel.
(3) The reactions can be carried out in a repeatable way and it is possible to average the spectra, which leads to better signal-noise ratio.

(4) It is possible to control the amounts of the compounds in reactions (meaning the ability to control the partial pressures of investigated compounds and their stabilities in time).
(5) Using the special inlet systems molecules with very low vapour pressure can also be investigated.[II]

A general overview of ICR-MS can be found in references 34,35.

Other methods used for gas-phase acidity or basicity investigations are high-pressure mass spectrometry (HPMS) and flowing after-glow mass spectrometry (FAG-MS).[36] Both these methods use considerably higher pressures compared to the ICR. This is an advantage from the point of view of reaching equilibrium but there is also the higher probability of side-reactions and the reactions can be followed for significantly shorter times than with ICR.

2.1.3 Gas-Phase Experimental Set-up

The *GB* values were determined using the Extrel FTMS 2001 FT-ICR mass spectrometer with 3.0 T superconductive magnet. Each equilibrium measurement is a measurement of relative basicity of bases B_1 and B_2 according to the Equations 3, 4 and 5. The ratio of the intensities of the $M+H^+$ ions in the mass spectrum was used as the estimate of the partial pressure ratio of the ions. M^+ isotope intensity corrections for $M+H^+$ intensities were made when necessary. The partial pressures of the neutrals were measured using the Bayard-Alpert gauge and were corrected for the differences in ionisation cross-sections (see ref 37 for details). The nominal pressures of the single neutral bases varied between 9×10^{-8} and 1.1×10^{-6} torr and the sum of pressures of the bases varied between 3.7×10^{-7} and 1.2×10^{-6} torr. The ratio of the ion intensities in the mass spectrum was used as the estimate of the ratio of numbers of the ions in the cell. The bases were introduced using two different sample introduction systems.

(1) The so-called "oven". The bases were introduced from the conventional sample introduction system, the so-called “oven”, that was maintained at 50–130°C using leak valves. Depending on particular compound it took several hours to several days to enter the ICR cell and achieve constant vapour pressure.
(2) The so-called direct inlet probe. This inlet system is the solution to the eternal problem with introduction of compounds with low volatility for which the oven is unsuitable due to the long path from the oven to the ICR cell. The direct inlet probe is a stainless steel rod with diameter around 1 cm. At its end there is a hole with 2 mm diameter to fix a capillary containing the compound under study. The rod can be inserted into the ICR spectrometer in such way that its tip is located at few centimetres from the cell (depending on the depth of introduction). This enables even compounds with very low volatility to reach the cell. The rod is inserted

through a differentially pumped vacuum chamber to prevent degradation of the vacuum in the ICR cell. Even the compounds that have low vapour pressures can be vaporized this way to yield sufficient vapour pressure in the cell. Constant partial pressures of the compounds were obtained by cooling or heating the probe tip. Temperature was taken up slowly, and the temperature was kept constant after the compound's pressure was at appropriate level. Probe tip cooling was achieved by letting cold nitrogen gas generated from liquid nitrogen flow through the cooling gas canal of the probe. Direct inlet probe tip temperatures and net system pressure for introducing each of these compounds are given in reference II Supporting Information Table S1.

For most compounds the equilibrium measurements were carried out at different partial pressures of the neutrals. Good agreement (difference mostly not more than 0.3 kcal·mol^{-1}) was obtained between the $\Delta\Delta G_b$ values at different ratios of partial pressures. At given partial pressures of the neutrals the equilibrium measurements were carried out as series of pulse sequences with different reaction times. Each sequence consisted of generating ions by an electron impact (20 eV) pulse from a few to 30 ms[II, III], giving them time to react and exciting and detecting the ions (see ref 37 for more details). From the ion intensity ratios at different reaction times (and at constant partial pressures of the neutrals) time plots were constructed. From the time plots it was found that between 1 and 30 s of reaction time was necessary to reach the equilibrium (depending on the reacting bases and their partial pressures). To ensure that the equilibrium has been reached reaction times significantly longer (at least 2 times longer) than what was required to reach the plateau on the time plot were used in all cases. All experiments in works II and III were carried out at cell temperatures 373 K.

2.2 UV-Vis Spectrophotometric Determination of ΔpK_a and ΔpK_{ip} Values

2.2.1 Acid-Base Equilibria in Condensed Media

Brønsted and Lowry created a theory that describes the proton transfer from acid HA^{z+1} to solvent S with forming of conjugate base A^z:

$$HA^{z+1} + S \underset{}{\overset{K_a}{\rightleftarrows}} A^z + SH^+ \qquad (6)$$

In case of neutral acid z = -1 and in case of neutral conjugate base z = 0.

Further studies of this reaction have shown that this acid dissociation equilibrium could be divided into several steps.[11] Thus the following consecutive

equilibria will set up when neutral acid HA^{z+1} (z = -1) reacts with solvent to give away proton:

$$HA^{z+1} + S \underset{}{\overset{K_1}{\rightleftarrows}} [HA^{z+1}\cdots S] \overset{K_2}{\rightleftarrows} [A^z\, SH^+] \overset{K_3}{\rightleftarrows} [A^z]\,[SH^+] \overset{K_4}{\rightleftarrows} A^z + SH^+ \qquad (7)$$

The first step is the initial complex formation between acid and solvent (K_1). This complex is usually hydrogen-bonded but when steric restrictions are present and/or the H–A bond in $[HA^{z+1}\cdots S]$ is weakly polar, the complex is held together by non-specific van der Waals forces. The next step (K_2) is the proton transfer from the acid to the solvent, which results in a *contact ion pair* complex $[A^z\, SH^+]$ formation. This step is called the primary ionisation step. The formed complex is also usually hydrogen-bonded but again, can be held together by electrostatic and/or van der Waals forces in the case of steric restrictions and/or delocalised charges of the formed ions. The next step is formation of the *solvent separated ion pair* $[A^z]\,[SH^+]$ (K_3), which is held together by Coulomb forces. This ion pair can dissociate into free ions (K_4). The overall product of these consecutive equilibrium constants: $K_1 \cdot K_2 \cdot K_3 \cdot K_4 = K_a$ expresses the acid strength of HA^{z+1}:

$$K_a = \frac{a(SH^+) \cdot a(A^z)}{a(HA^{z+1})} \qquad (8)$$

Here the *a* values are the activities of the corresponding spieces. The negative logarithm pK_a is usually used as a measure of the strength of an acid HA^{z+1} in particular medium:

$$pK_a = -\log \frac{a(SH^+) \cdot a(A^z)}{a(HA^{z+1})} \qquad (9)$$

In solvents with good ability to separate and stabilise both anions and cations, the situation where these are separated, is favoured. Otherwise, the situation is more complicated and ion pairing and/or aggregation should always be considered as a possibility.[11]

Ion pairing depends on the solvent properties, size of the ions and the charge distribution in ions, hydrogen bonding and specific solvation possibility, The general trend is that small ions tend to form solvent-separated ion-pairs (SSIP) while large ions with delocalised charge tend to form contact ion-pairs (CIP). Increase in ion-solvating and ions-separating power of the solvent favours formation of the solvent-separated ion-pairs. In the case of extensive ion-pairing it is difficult to measure the pK_a values that refer to free ions. In this case usually relative ion pair acidity ΔpK_{ip} is investigated instead (see equations 18, 19 and 20).

In media of poor ability to solvate ions (in particular polar aprotic solvents) in addition to ion-pairing there are additionally two important side reactions called homo- (eq 10) and heteroconjugation (eq 11):[38]

$$A_1^z + HA_1^{z+1} \quad \rightleftarrows \quad \left[A_1 \cdot\cdot HA_1\right]^{2z+1}, \tag{10}$$

$$A_1^z + HA_2^{z+1} \quad \rightleftarrows \quad \left[A_1 \cdot\cdot HA_2\right]^{2z+1}. \tag{11}$$

It is generally observed that the extent of homoconjugation increases with increasing number of acidic hydrogen atoms in the acid molecule. Poor steric hindrance of the protonation/deprotonation centre is also a source of increased homoconjugation.[38] The easiest way to decrease the influence of the association processes on acid-base equilibria without changing the medium is to use methods that allow to work with very dilute solutions.

2.2.2 The Role of Solvent on Acid-Base Reactions

As it already appeared in the previous section, several medium properties have an important influence on the acid-base reactions in condensed media. From these, in combination with the solute molecule properties (charge and its localization/delocalization, polarity, polarizability etc.) and on the mole ratio (concentration) of solvent(s) and the solute(s) depends the character of the results (solubility, ionisation, dissociation, aggregation etc.) of its interactions with the solvent and other solutes.[11]

The dielectric constant (D) of a solvent describes its ability to reduce the coulombic interaction between charged particles in solution, to separate or to *dissociate* ion pairs and to orient dipole molecules. Solvents with large D ($D \geq 40$) are called *polar* and ionic species are fully dissociated in them. In solvents of intermediate dielectric constant (D = 15 .. 40) the ratio between free and associated ions depends on the structure of the solvent as well as on the concentration and properties of the ionic compounds (e.g. ion size, charge distribution, hydrogen-bonding abilities, etc.). Solvents with low D are called *apolar* or *nonpolar*.[11]

One of the most important solvent properties in acid-base chemistry — *ionising power* of the solvent — depends mainly on the ability of the solvent to be an electron pair acceptor (EPA) or electron pair donor (EPD). These properties are empirically described with donor numbers (*DN*) and acceptor numbers (*AN*). Higher values mean that solvent has higher ability to ionise neutral ionogen molecules and to stabilise the ions formed. For example, if the solvent is a good EPD but poor EPA it stabilises cations efficiently but anions poorly and anions tend to form aggregates with cations or neutrals described in previous section.

Table 1. Parameters Characterising Solvent for Acidy or Basicity Investigations[a].

Solvent	*DN*[b]	*AN*[c]	*D*[d]	pK_{auto}[e]
Tetrahydrofuran	20.0	8.0	7.58 7.47[f,g]	34.7[h]
***n*-Heptane**		(0.0 for n-hexane)	1.92[f], 1.94[f,g]	
Acetonitrile	14.1	18.9	35.94	≥33.3
Dimethyl sufoxide	29.8	19.3	46.45 46.71[f,g]	33.3
Water		54.8	78.30	14.00

a — if not mentioned otherwise, all the values in Table 1 are from ref. 11, *b* — donor number (kcal·mol^{-1}), *c* — acceptor number, *d* — dielectric constant, *e* — autoprotolysis constant pK_{auto} = –log(K_{auto}), unit of K_{auto} is (mol^2·l^{-2}), *f* — at 20°C, *g* — values from ref. 10, *h* — estimated value from ref. 39.

Brønsted *acid-base properties* of the solvent have also important influence on the strengths of acids and bases. Solvent's ability to donate (eq 12) or accept (eq 13) a proton characterises these properties:

$$SH \rightleftarrows H^+ + S^- \quad (12)$$

$$SH + H^+ \rightleftarrows SH_2^+ \quad (13)$$

A combination (eq 14) of these processes is described quantitatively by the autoprotolysis constant (K_{auto}) of the solvent:

$$2\ SH \overset{K_{auto}}{\rightleftarrows} SH_2^+ + S^- \quad (14)$$

The lower is the K_{auto}, the wider is the range of acid and/or base strengths that can exist in the solvent. If the solvent molecule has no protons at all or ionisation according to the reaction in eq 12 is negligible then the solvent is called *aprotic*, if the acid dissociation of the solvent proceeds to a measurable extent then the solvent is called *protic*. In *amphiprotic* solvent both reactions (eqs 12 and 13) are present. Low acidity and basicity make a solvent a good *differentiating* solvent. Significantly acidic or basic nature of a solvent makes it a *levelling* solvent in terms of acidity or basicity, respectively.[11]

Hydrogen bonding plays a particularly important role in the interactions between ions and solvents. The stronger are the hydrogen-bond acceptor (HBA) properties of a solvent the better it stabilizes cations. The stronger the hydrogen-bond donor (HBD) properties of a solvent the better it stabilizes anions.

The combination of these three groups of solvent properties — ionising power, dissociative power and acid-base properties and the nature of solute molecules determine the nature of acid-base behaviour of a particular compound in a particular solvent.

Water is by far the most popular solvent for acid-base equilibria investigation. With its high EPD-EPA ability, high dielectric constant (D = 78.30[11]) and relatively high acidity and basicity (pK_{auto} = 14.00[11]) it is a good ionising and dissociating solvent. At the same time it is also a levelling solvent for both strong acids and strong bases. Water is very eager to form hydrogen-bonded complexes and thus it largely masks the intrinsic acid-base properties of acids and bases.

Acetonitrile (AN) has many properties that make it suitable as a medium for acid-base studies. It has low basicity and very low ability to solvate anions.[38] The low basicity gives AN an advantage over the other very popular solvent for acid-base studies — DMSO — which is considerably more basic (stronger acceptor of hydrogen bond). AN has high dielectric constant (D=35.94[11]) and hence favours the dissociation of ion pairs into free ions. The autoprotolysis constant of AN is very low: $pK_{auto} \geq 33$,[40] (even values of pK_{auto} as high as 44 have been suggested[41,42]). This makes it a good differentiating solvent, especially for strong acids.[22,23,24] AN is a weak electron-pair donor (DN =14.1[11]) and totally lacks the HBD ability. Hence, it solvates cations better than anions.[11,38] AN has the disadvantage that very strong bases tend to oligomerize this solvent.[38,41] Still, AN has shown itself as a sufficiently good medium for investigation of bases even as strong as P_3-phosphazenes (for 4-MeO-$C_6H_4P_3$(dma) the pK_a(AN) is 31.99).[25] Additional advantages of AN are its transparency in the UV region down to 190 nm and relative ease of purification.

Tetrahydrofuran (THF) is by its differentiating ability (estimated pK_{auto} = 34.7[39]) similar to AN. It solvates cations (DN = 20.0[11]) better than AN, but it solvates anions even more poorly than AN. It has low dielectric constant (D = 7.58[11]). As a result, in THF the ion-pairing processes are much more favoured than in AN and even at low concentrations the ion-pairing processes must be considered. THF is much more resistant to the superbases and at least 8 orders of magnitude stronger bases can be studied in THF than in AN.[41] Recently, quite some studies on basicity in THF have been published.[15–18] Also, numerous acidity studies, mostly focused on CH-acids, have been carried out in THF.[19–21]

Heptane has many disadvantages from the point of view of acid-base equilibria studies. Ionic compounds have very low solubilities in heptane (D = 1.92)[11]. Ions form aggregates in heptane — ion pairs and higher aggregates, such as tetramers, hexamers etc. Neutral molecules also tend to associate with each other and ion complexes.[28,I] Heptane is incapable of deprotonating or protonating without further reactions, therefore its pK_{auto} is not measurable. This is also the reason why only relative acidity values of ΔpK_{ip} can be measured in heptane. Still, it is of considerable interest to perform acidity measurements in

solvents with $D < 2$ because $D = 2$ is a kind of half-way between polar solvents and the gas phase ($D = 1$). Acidity data in solvents of low polarity are also very valuable for many other reasons: [28] (1) The acidity of a compound in a given medium is influenced by both electronic effects of the substituents and the solvent effects of the medium. In polar solvents the solvent effects are strong and analysis of the acidity data in terms of electronic effects is difficult. In nonpolar solvents the medium has less influence on the acidities and the acidities are better differentiated. (2) Systems of extremely high acidity can be studied in nonpolar solvents. (3) Acidities of very weak acids can be measured in nonpolar solvents. (4) Many processes in organic synthesis and in the chemical industry involving acids and bases are carried out in nonpolar media, and acidity data in nonpolar media are needed to be able to understand and to quantitatively describe these processes.

In an earlier work Leito et al. managed to establish the conditions for investigation of acid-base equilibria in heptane and to compile a preliminary acidity scale in heptane.[28] In paper I was published an expanded acidity scale in heptane.

2.2.3 Methods of pK_a Determination in Condensed Media

There is no universal method that is able to describe quantitatively all the processes appearing in the studies of acid-base equilibria in condensed media. Several methods have been developed and described,[43,44] their applicability and advantages over others depend on properties of solvent and compounds under study. It is obvious that the combined use of different methods gives more and reliable information, thus the combined use, if possible, is preferred. On choosing the appropriate method or combination of methods thorough analysis of the particular system should be carried out on keeping in mind an ultimate goal. Undesirable side-reactions and effect of impurities are only few aspects to consider besides the others mentioned in previous sections. Here only the main methods used for studying of acid-base equilibria in aprotic dipolar media are briefly discussed.

UV-Vis spectrophotometric methods base on the UV-Vis radiation absorption difference of acid (or base) and its conjugate base (or acid) forms. The exact analytical concentrations of compounds are usually not needed. The extent of association processes, if present, has to be determined with other methods. Advantages of UV-Vis spectrophotometry are that very low concentrations can be used and thus in several solvents of poor ability to stabilise ions the picture of association processes is simpler than with the above methods. Undesirable side reactions generally affect the UV-Vis spectra of the system and their presence can be determined. A disadvantage of UV-Vis spectrophotometry is that compounds must have difference in light absorption spectra of

acid (or base) and conjugate base (or acid). Also the solvent used must be transparent in the analytical wavelength region. The results of these methods can be sensitive to the acidic and basic impurities.

Several other experimental techniques have found application, let only mention some of these: *potentiometry, conductometric methods, NMR, IR*. All these methods have at least one of two disadvantages compared with UV-Vis spectrophotometry: either the need of higher concentrations of solutes (which means the higher possibility of associations) or need of matrixes instead of pure solvents as the investigation media.

Besides the experimental techniques intensive work is in progress to describe or at least to estimate the processes and their extent arising on acid-base equlibria in condensed media with *quantum chemistry and correlation methods*.[45] The crucial problem of quantum chemistry methods is the very high computing power necessary to take into account all electronic, steric and medium effects. The situation of theoretical gas-phase acid-base studies is much better as this medium is virtually free from medium effects. These methods supplement the overall picture and there is no doubt that in the future these methods take an equivalent place beside or probably override the traditional methods in describing the acid-base equilibria in condensed media.

2.2.4 UV-Vis Spectrophotometric Method for ΔpK_a and ΔpK_{ip} Determination

It was said in the section 2.2.3 that UV-Vis spectrophotometric methods have several advantages over others. To exclude the necessity for measuring the hydrogen ion activity (see eq 7) a UV-Vis spectrophotometric method is developed.[14,24,25,28] In this method proton distribution equilibrium between two compounds HA_1^{z+1} and HA_2^{z+1} respectively, is studied:

$$HA_2^{z+1} + A_1^{z} \overset{K}{\rightleftarrows} A_2^{z} + HA_1^{z+1} \qquad (15)$$

The negative logarithm of the equilibrium constant K measures the difference of acidities of the neutral acids (z = –1) or protonated forms of neutral bases (z = 0) HA_1^{z+1} and HA_2^{z+1} at given conditions:

$$\Delta pK_a = pK_a(HA_2^{z+1}) - pK_a(HA_1^{z+1}) = -\log K = \log \frac{a(A_1^{z}) \cdot a(HA_2^{z+1})}{a(HA_1^{z+1}) \cdot a(A_2^{z})} \qquad (16)$$

The ratios of basic and acidic forms of the compounds in eq 16 are known as indicator ratios:

$$\mathrm{I}_1 = \frac{a(\mathrm{A}_1^z)}{a(\mathrm{HA}_1^{z+1})} \quad \text{and} \quad \mathrm{I}_2 = \frac{a(\mathrm{A}_2^z)}{a(\mathrm{HA}_2^{z+1})}. \tag{17}$$

From the eq 16 it appears that when measuring the relative acidities of two compounds then there is no need to measure the activity of the hydrogen ion $a(\mathrm{SH}^+)$.

In the solvents with low or medium polarity (heptane and THF) the consideration for the ions to be fully ion-paired is made.[I,II,III] As an example, in the case of THF, the proton distribution equilibrium between two bases B_1, B_2 and titrant acid $\mathrm{A}^-\mathrm{H}^+$ can be presented in the following form:

$$\mathrm{B}_2 + \mathrm{HB}_1^+\mathrm{A}^- \overset{K_d^{\mathrm{HB}_1^+\mathrm{A}^-}}{\rightleftarrows} \mathrm{B}_2 + \mathrm{HB}_1^+ + \mathrm{A}^- \overset{K_\alpha}{\rightleftarrows} \mathrm{HB}_2^+ + \mathrm{B}_1 + \mathrm{A}^- \overset{1/K_d^{\mathrm{HB}_2^+\mathrm{A}^-}}{\rightleftarrows} \mathrm{HB}_2^+\mathrm{A}^- + \mathrm{B}_1 \tag{18}$$

The constants K_d are the dissociation constants of the respective ion pairs. The directly measured quantity is the relative ion-pair basicity — $\Delta\mathrm{p}K_\mathrm{ip}$ — of bases B_1 and B_2. It is expressed as follows:

$$\Delta\mathrm{p}K_\mathrm{ip} = \mathrm{p}K_\mathrm{ip}(\mathrm{HB}_2^+\mathrm{A}^-) - \mathrm{p}K_\mathrm{ip}(\mathrm{HB}_1^+\mathrm{A}^-) = \log\frac{K_\alpha \cdot K_d^{\mathrm{HB}_1^+\mathrm{A}^-}}{K_d^{\mathrm{HB}_2^+\mathrm{A}^-}} = \log\frac{a(\mathrm{HB}_2^+\mathrm{A}^-)\cdot a(\mathrm{B}_1)}{a(\mathrm{HB}_1^+\mathrm{A}^-)\cdot a(\mathrm{B}_2)} \tag{19}$$

In the case acidities in heptane equations for two acids HA_1, HA_2 and titration base B, analogically to equations 18 and 19, can be written out.[I]

If the K_d values can be measured or estimated then the $\Delta\mathrm{p}K_\alpha$ (an estimate of the $\Delta\mathrm{p}K_\mathrm{a}$) can be found as follows:

$$\Delta\mathrm{p}K_\alpha = \mathrm{p}K_\alpha(\mathrm{HB}_2^+) - \mathrm{p}K_\alpha(\mathrm{HB}_1^+) = \Delta\mathrm{p}K_\mathrm{ip} - \log\frac{K_d^{\mathrm{HB}_1^+\mathrm{A}^-}}{K_d^{\mathrm{HB}_2^+\mathrm{A}^-}} \tag{20}$$

The convenient and common experimental technique to study ion-pairing processes is combined use with conductometry[46] but also theoretical estimation of ion-pair dissociation constant K_d using Fuoss equation (eq 21) has been used[15].

$$K_\mathrm{d} = \frac{3000\cdot e^b}{(4\pi N a^3)} \quad \text{,where} \quad b = \frac{-e^2}{aDkT}\,, \tag{21}$$

$N = 6.02 \times 10^{-23}$ mol^{-1}, a is the distance of ion centres in centimetres ($a = r^+ + r^-$), e is the charge of electron 4.80×10^{-10} esu (1 esu = 1.60×10^{-19} C) and Boltzmann constant $k = 1.38 \times 10^{-16}$ erg · K^{-1} (1.38×10^{-23} J · K^{-1}). Using the K_d value an estimate of $\Delta pK_a - \Delta pK_\alpha$ is then obtained.

Advantages and disadvantages of the UV-Vis spectrophotometric method. The presence of the two compounds in the same solution eliminates many possible sources of error or reduces their influence: (1) The disturbing effects (traces of water in the medium, concentration errors) affect both compounds with the same magnitude and are expected to partially cancel out. Thus one can expect that the effect of traces of water on the measurements will be less pronounced than in such measurements where pK_a of a single compound is measured at a time. (2) The solutions can be very dilute in certain cases (π-electron rich systems conjugated with acidity centre) to lower the extent of unwanted competing equilibria or to clarify the picture. (3) Low concentrations allow use of very weak buffering with this method. If a minor acidity change of the solution occurs, it will affect both of the compounds and its effect will cancel out. (4) An important point is that the method eliminates the need for quantitative measurement of acidity of the medium. (5) In the case of "visible" compounds (i.e. compounds with good absorbance in UV-Vis wavelength area), concentrations of solutions must be known only approximately, for maximum absorbances to fall into the range of 0.5 to 1.2 AU on applicable wavelengths. In any case, solutions with very low concentrations can be used if one of two compounds is "visible" and satisfying uncertainty of concentrations (i.e. weighing) is guaranteed.

A disadvantage of the method is that acid-base properties of only such compound pairs can be measured where at least one of compounds absorbs in the UV-Vis spectral region and the spectra of the acid and the base forms are different at least in details. Also the pK_a-s of the compounds must not be very different from each other (depending on solvent, preferably not more than 1.2–2 pK_a units).

2.2.5 Calculation Methods for UV-Vis Spectrophotometric ΔpK_a and ΔpK_{ip} (ΔpK_α) Determination Methods

General essence of calculation methods of UV-Vis spectrophotometric method are outlined here. As an example, calculation methods for free ions (as in the case of AN) are demonstrated here. In case of ion-pair acidity and basicity calculations the method is generally the same.[I,II,III]

According to the Lambert-Beer law the absorbance A_x^λ of compound X in a layer of unit thickness at wavelength λ expresses as follows:

$$A_{\mathrm{X}}^{\lambda} = [\mathrm{X}]\varepsilon_{\mathrm{X}}^{\lambda} \tag{22}$$

where ε_x^{λ} is a molar absorbance coefficient at given wavelength. If in solution is two partially dissociated acids (that is four separate compounds), then at wavelength λ expresses the net absorbance assuming the solvent absorbance is compensated:

$$A^{\lambda} = [\mathrm{HA}_1^{z+1}]\varepsilon_{\mathrm{HA}_1^{z+1}}^{\lambda} + [\mathrm{A}_1^{z}]\varepsilon_{\mathrm{A}_1^{z}}^{\lambda} + [\mathrm{HA}_2^{z+1}]\varepsilon_{\mathrm{HA}_2^{z+1}}^{\lambda} + [\mathrm{A}_2^{z}]\varepsilon_{\mathrm{A}_2^{z}}^{\lambda} \tag{23}$$

If we take a net concentration of acid and base form equal to one, we can express the concentration of acid forms:

$$[\mathrm{HA}_1^{z+1}] = 1 - [\mathrm{A}_1^{z}] \tag{24}$$

$$[\mathrm{HA}_2^{z+1}] = 1 - [\mathrm{A}_2^{z}] \tag{25}$$

and the eq 23 can be rearranged:

$$A^{\lambda} = \varepsilon_{0\mathrm{HA}_1^{z+1}}^{\lambda} + \varepsilon_{0\mathrm{HA}_2^{z+1}}^{\lambda} + [\mathrm{A}_1^{z}](\varepsilon_{0\mathrm{A}_1^{z}}^{\lambda} - \varepsilon_{0\mathrm{HA}_1^{z+1}}^{\lambda}) + [\mathrm{A}_2^{z}](\varepsilon_{0\mathrm{A}_2^{z}}^{\lambda} - \varepsilon_{0\mathrm{HA}_2^{z+1}}^{\lambda}) \tag{26}$$

Here, $\varepsilon_{0x}^{\lambda}$ is a normalised absorbance coefficient at given wavelength.

If we take the normalised absorbance coefficients of pure acid forms to the left side of the equation and divide both sides of the equation with $(\varepsilon_{0\mathrm{A}_2^{z}}^{\lambda} - \varepsilon_{0\mathrm{HA}_2^{z+1}}^{\lambda})$, we get:

$$\frac{A^{\lambda} - \varepsilon_{0\mathrm{HA}_1^{z+1}}^{\lambda} - \varepsilon_{0\mathrm{HA}_2^{z+1}}^{\lambda}}{(\varepsilon_{0\mathrm{A}_2^{z}}^{\lambda} - \varepsilon_{0\mathrm{HA}_2^{z+1}}^{\lambda})} = [\mathrm{A}_1^{z}]\frac{(\varepsilon_{0\mathrm{A}_1^{z}}^{\lambda} - \varepsilon_{0\mathrm{HA}_1^{z+1}}^{\lambda})}{(\varepsilon_{0\mathrm{A}_2^{z}}^{\lambda} - \varepsilon_{0\mathrm{HA}_2^{z+1}}^{\lambda})} + [\mathrm{A}_2^{z}] \tag{27}$$

This equation describes the line with a slope $[\mathrm{A}_1^{z}]$ and intercept $[\mathrm{A}_2^{z}]$. At given wavelength all the ε_0^{λ}-s are constant and are easy to determine from the spectra of solutions of pure acid and base forms of compounds. At different wavelengths of solution of certain acidity are all the members except concentrations in equation 27 variables and with regression analysis the latter ones are determinable. Using the normalized concentrations from eq-s 24 and 25 and equation 16 we get:

$$\Delta \mathrm{p}K_{\mathrm{a}} = \log\frac{[\mathrm{H}^+][\mathrm{A}_1^{z}]}{(1-[\mathrm{A}_1^{z}])} - \log\frac{[\mathrm{H}^+][\mathrm{A}_2^{z}]}{(1-[\mathrm{A}_2^{z}])} = \log\frac{[\mathrm{A}_1^{z}](1-[\mathrm{A}_2^{z}])}{(1-[\mathrm{A}_1^{z}])[\mathrm{A}_2^{z}]} \tag{28}$$

The method is universal, but to employ it one needs spectra of pure acid and base forms of the compounds to determine corresponding ε_0^{λ}-s. Also one needs to know the ratio of concentrations of compounds in mixture and pure forms.

Sometimes, depending on spectra of compounds, it is possible to use very simple and elegant calculation methods to get indicator ratios. On the simpler cases one needs only the spectra of acid and base form of the mixtures and a set spectra of mixtures of variable acidity. Some examples of different cases are given here.

a) If there is a wavelength λ, at which neither forms of one compound do not absorb and basic form of second compound absorb

$$\varepsilon^{\lambda}_{0\mathrm{HA}_1^{z+1}} = \varepsilon^{\lambda}_{0\mathrm{HA}_2^{z+1}} = \varepsilon^{\lambda}_{0\mathrm{A}_2^{z}} = 0 \quad \text{and} \quad \varepsilon^{\lambda}_{0\mathrm{A}_1^{z}} \neq 0$$

then the eq 26 simplifies:

$$A^{\lambda} = [\mathrm{A}_1^{z}]\varepsilon^{\lambda}_{0\mathrm{A}_1^{z}} \tag{29}$$

and the indicator ratio expresses then:

$$\frac{[\mathrm{A}_1^{z}]}{[\mathrm{HA}_1^{z+1}]} = \frac{A^{\lambda}}{A^{\lambda}_{\mathrm{A}^{z}} - A^{\lambda}} \tag{30}$$

A^{λ} is absorbance of solution where both compounds are in acid and base form and $A^{\lambda}_{\mathrm{A}^{z}}$ is absorbance of solution having both compounds in base form. If one of two compounds here is mainly "invisible", the concentrations of acids and titrant base should be known as well and calculation of relative acidity bases on classical $\Delta \mathrm{p}K_a$ calculation.

b) If one compound has an isosbestic point at certain wavelength (that is both acid an base form have same absorbance coefficients) and only basic form of second compound absorbs

$$\varepsilon^{\lambda}_{0\mathrm{HA}_2^{z+1}} = \varepsilon^{\lambda}_{0\mathrm{A}_2^{z}} \neq 0 \neq \varepsilon^{\lambda}_{0\mathrm{A}_1^{z}} \quad \text{and} \quad \varepsilon^{\lambda}_{0\mathrm{HA}_1^{z+1}} = 0$$

then eq 26 simplifies:

$$A^{\lambda} = [\mathrm{A}_1^{z}]\varepsilon^{\lambda}_{0\mathrm{A}_1^{z}} + \varepsilon^{\lambda}_{0\mathrm{HA}_2^{z+1}} . \tag{31}$$

The indicator ratio of second compound expresses then as follows:

$$\frac{[\mathrm{A}_1^{z}]}{[\mathrm{HA}_1^{z+1}]} = \frac{A^{\lambda} - A^{\lambda}_{\mathrm{HA}^{z+1}}}{A^{\lambda}_{\mathrm{A}^{z}} - A^{\lambda}} \tag{32}$$

$A^{\lambda}_{\mathrm{HA}^{z+1}}$ is here a net absorbance of mixture solution where both compounds are in acid forms.

c) If there is a spectrum of the mixture where both compounds are in base form then the net absorbance from eq 23 we get:

$$A^{\lambda} = [\mathrm{A}_1^{z}]\varepsilon^{\lambda}_{0\mathrm{A}_1^{z}} + [\mathrm{A}_2^{z}]\varepsilon^{\lambda}_{0\mathrm{A}_2^{z}} \tag{33}$$

The rightsided members of this eq can be expressed as absorbances of pure compounds in base forms multiplied by coefficients b_n:

$$[\mathrm{A}_1^{z}]_{\mathrm{mixture}}\,\varepsilon^{\lambda}_{0\mathrm{A}_1^{z}} = \mathrm{b}_1^{\mathrm{A}^{z}}\; A^{\lambda}_{\mathrm{A}_1^{z}\,\mathrm{pure}} \tag{34}$$

and

$$[\mathrm{A}_2^{z}]_{\mathrm{mixture}}\,\varepsilon^{\lambda}_{0\mathrm{A}_2^{z}} = \mathrm{b}_2^{\mathrm{A}^{z}}\; A^{\lambda}_{\mathrm{A}_2^{z}\,\mathrm{pure}} \tag{35}$$

These coefficients $\mathrm{b}_n^{\mathrm{A}^{z}}$ are constant over the wavelength range, where ε^{λ}-s do not equal to zero. From the combination of eq-s 33, 34 and 35 is possible to calculate from the spectrum of the mixture of compounds in base form, and from the spectra of both compounds in base form coefficients $\mathrm{b}_1^{\mathrm{A}^{z}}$ and $\mathrm{b}_2^{\mathrm{A}^{z}}$ using least squares minimization over a wavelength range by minimising S_p:

$$\mathrm{S_p} = \sum_{\lambda}\left[A^{\lambda} - \left(\mathrm{b}_1^{\mathrm{A}^{z}}\; A^{\lambda}_{\mathrm{A}_1^{z}\,\mathrm{pure}} + \mathrm{b}_2^{\mathrm{A}^{z}}\; A^{\lambda}_{\mathrm{A}_2^{z}\,\mathrm{pure}}\right)\right]^2 \tag{36}$$

These coefficients $\mathrm{b}_1^{\mathrm{A}^{z}}$ and $\mathrm{b}_2^{\mathrm{A}^{z}}$ show the ratio of concentrations in mixture and pure forms. Analogously the absorbance of the mixture solution where both compounds are in acid and base form by combining eq-s 26, 22, 34, 35 and introducing for both compounds a dissociation level α_n, which shows the ratio of base form concentration ($[\mathrm{A_x}^{z}]$) to analytical concentration ($[\mathrm{A_x}^{z}]+[\mathrm{HA_x}^{z+1}]$) we get:

$$A^{\lambda} = \mathrm{b}_1^{\mathrm{A}^{z}} A^{\lambda}_{\mathrm{HA}_1^{z+1}\,\mathrm{pure}} + \mathrm{b}_2^{\mathrm{A}^{z}} A^{\lambda}_{\mathrm{HA}_2^{z+1}\,\mathrm{pure}} + \alpha_1 \mathrm{b}_1^{\mathrm{A}^{z}}\left(A^{\lambda}_{\mathrm{A}_1^{z}\,\mathrm{pure}} - A^{\lambda}_{\mathrm{HA}_1^{z+1}\,\mathrm{pure}}\right) + \alpha_2 \mathrm{b}_2^{\mathrm{A}^{z}}\left(A^{\lambda}_{\mathrm{A}_2^{z}\,\mathrm{pure}} - A^{\lambda}_{\mathrm{HA}_2^{z+1}\,\mathrm{pure}}\right) \tag{37}$$

from this eq using the least squares minimisation over the wavelength range described in eq 36 by minimising S_s respective α_1 and α_2 for compounds at different acidities are found

$$\mathrm{S_s} = \sum_{\lambda}\left\{A^{\lambda} - \mathrm{b}_1^{\mathrm{A}^{z}} A^{\lambda}_{\mathrm{HA}_1^{z+1}\,\mathrm{pure}} - \mathrm{b}_2^{\mathrm{A}^{z}} A^{\lambda}_{\mathrm{HA}_2^{z+1}\,\mathrm{pure}} - \left[\alpha_1 \mathrm{b}_1^{\mathrm{A}^{z}}\left(A^{\lambda}_{\mathrm{A}_1^{z}\,\mathrm{pure}} - A^{\lambda}_{\mathrm{HA}_1^{z+1}\,\mathrm{pure}}\right) + \alpha_2 \mathrm{b}_2^{\mathrm{A}^{z}}\left(A^{\lambda}_{\mathrm{A}_2^{z}\,\mathrm{pure}} - A^{\lambda}_{\mathrm{HA}_2^{z+1}\,\mathrm{pure}}\right)\right]\right\}^2 \tag{38}$$

These α_1 and α_2 are substituted to eq 16 and the ΔpK_a expresses then:

$$\Delta pK_a = \log \frac{\alpha_1(1-\alpha_2)}{(1-\alpha_1)\alpha_2}. \quad (39)$$

This so called least-squares of linear combination method is universal and can be used when compounds have overlapping absorbances, the only limit is that, the spectra must not be identical. From our experiments we have concluded that if the compounds have similar shape absorbance spectra but the difference of absorbance maxima is at least 6 nm, then this calculation method is usually well applicable. From UV-Vis spectrophotometric data it is possible to calculate with good confidence level ΔpK_a values up to 2.5 units. Usually the ΔpK_a values obtained using different data treatment methods agreed well. The raw spectrophotometric data was imported to and calculations were done in spreadsheet calculation program MS EXCEL.

2.2.6 Experimental Set-up for UV-Vis Spectrophotometric Titrations

All procedures involved with preparation of solutions and acid-base titrations were carried out in a commercial glovebox under an atmosphere of argon. Because of slow dissolution of the substances in heptane and some cases in THF, the vials of stock solutions were tightly closed, removed from the glovebox, sonicated in an ultrasonic bath for around 10 to 30 min and transferred back to the glovebox.

The atmosphere in the glovebox was constantly circulated through a purification system containing activated carbon, molecular sieves, and activated copper for removal of residues of volatile organics, water vapour, and oxygen, respectively. The residual concentrations of water and oxygen in the atmosphere of the glovebox during the measurements were constantly monitored and were at or below 1 ppm.

For spectrophotometric titration, a commercial spectrometer equipped with an external sample compartment positioned in the glovebox was used. The external sample compartment was connected to the spectrometer via quartz fiber-optic cables. The temperature in the external sample compartment was constantly monitored. The temperature was always between 25.0 and 28.5°C.

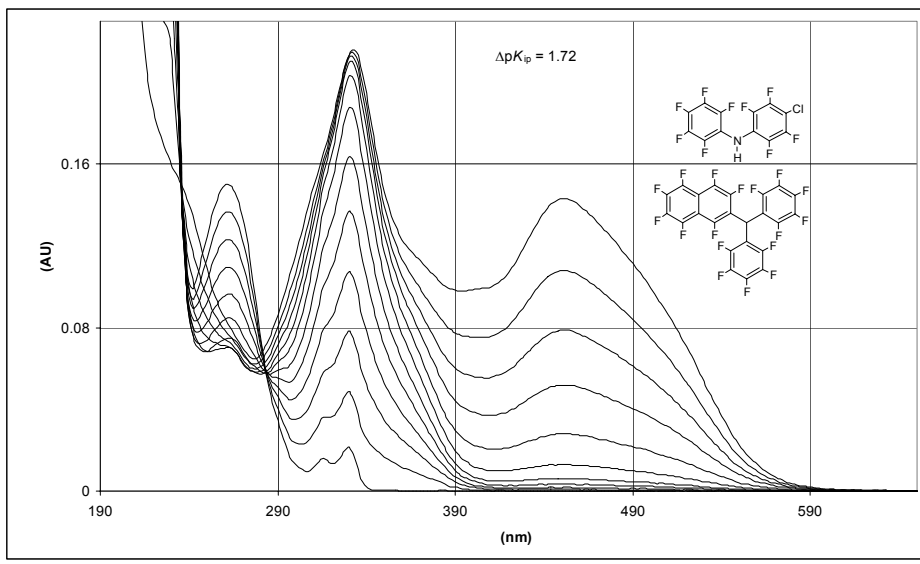
Usually all solutions were used within 3 days, but in a few cases solutions as old as 5 days were used. In these particular cases, no deviations during of the titration experiment from the usual behaviour were observed.

Working solutions were prepared gravimetrically by dilution of the stock solution. Vials and pipettes used in work were washed with ethanol before

heating in an oven at 150°C for at least 5 h and were then immediately transferred to the glovebox.

The mixture solution of acids or bases as well as both solutions of acids or bases separately was titrated with an optically transparent acid and/or base solution and the data for $\Delta pK_{a/ip}$ calculations was obtained from UV-Vis spectra (corrected for dilution). From each titration experiment, the $\Delta pK_{a/ip}$ was determined as the mean of 5–25 values (see Figure 1), calculated from spectra of varied medium acidity.

Figure 1. UV-Vis Spectra of Titrated Mixture Solution of Two Acids in Heptane.



2.3 Theoretical Gas-Phase Basicity Calculation and Estimation of Basicity Contributions

2.3.1 Calculations of Gas-Phase Basicities

The quantum-chemical calculations reported in works II and III were carried out using the Gaussian 2003 series of programs.[47] Density functional theory (DFT) calculations were performed using the B3LYP hybrid functional. Full geometry optimisations and vibrational analyses were performed using the 6–311+G** basis set. This approach has been demonstrated to describe the gas-phase basicities of a wide variety of relatively simple molecules with reasonable accuracy[9,48]. All stationary points were found to be true minima (N_{imag} = 0).

Unscaled B3LYP 6–311+G** frequencies were used to calculate the gas-phase basicities (*GB*) and proton affinities (*PA*) 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.

In work III, for protonated diamines (DAH^+) with the possibility of intramolecular hydrogen bond (HB) formation two conformers were calculated: one with hydrogen bond DAH^+_{HB} and the other without hydrogen bond DAH^+_{NHB}, where HB formation was not allowed by using the straight chain or *trans-trans* conformation of DAH^+. In cases where nonbonded conformer was more stable the most stable hydrogen-bonded conformer was also calculated. Detailed information of gas-phase basicity and proton affinity calculations can be found in Table S5 in SI of reference III.

2.3.2 Calculations of Basicity Contributions Using the Isodesmic Reactions Method

In work III, the method of isodesmic reactions described in ref 49 was used to estimate the energetic contributions on the basicity of the studied diamines. The example of isodesmic reactions is presented on Figure 11 (Section 5.2). For each type of diamines two isodesmic reactions are used: one for estimating the strain energy *SE*(DA) in the neutral diamine DA and the other for estimating the joint contribution of strain energy and hydrogen bond energy [*HB*(DAH^+) + *SE*(DAH^+)] (below termed also as $(HB+SE)^+$) in the protonated diamine DAH^+. These contributions were found as follows:

$$SE(\mathrm{DA}) = H(\mathrm{DA}) + \mathrm{x} \cdot H(\mathrm{HC}) - H(\mathrm{MA_1}) - H(\mathrm{MA_2}) \quad (40)$$

$$[HB(\mathrm{DAH^+}) + SE(\mathrm{DAH^+})] = H(\mathrm{DAH^+}) + \mathrm{x} \cdot H(\mathrm{HC}) - H(\mathrm{MA_1H^+}) - H(\mathrm{MA_2H}) \quad (41)$$

The number of hydrocarbons (HC) participating in the reaction is denoted by x. MA_1, MA_2 are the respective monoamines. The monoamine that is a stronger base is denoted by MA_1. The enthalpies of diamines (*H*(DA)), their protonated forms (*H*(DAH^+)), hydrocarbons (*H*(HC)), monoamines (*H*(MA)) and protonated monoamines (*H*(MAH^+)) were found computationally as described above. The treatment can in principle be carried out either in terms of enthalpy or free energy. In work III the enthalpy was chosen in order to avoid the complications arising from the large entropy effects that are present if the number of molecules changes in the course of the reaction or if a cycle opens or closes and also in order to facilitate comparison with earlier works.

For splitting the joint contribution [*HB*(DAH^+) + *SE*(DAH^+)] into components the intramolecular hydrogen bond energy *HB*(DAH^+) is found as de-

scribed in ref 49 from model systems presented in Figure 12 according to the following equation:

$$HB(\mathrm{DAH^+}) = H(\mathrm{R^1R^2R^3NH^+\cdots NR^4R^5R^6}) - H(\mathrm{R^1R^2R^3NH^+}) - H(\mathrm{NR^4R^5R^6}) \quad (42)$$

Where $\mathrm{R^1R^2R^3NH^+\cdots NR^4R^5R^6}$ is a model hydrogen-bonded complex obtained from the respective protonated diamine by freezing the geometry of the hydrogen bond and reducing the alkyl fragments to small size in order to avoid their steric interaction. The species $\mathrm{R^1R^2R^3NH^+}$ and $\mathrm{NR^4R^5R^6}$ are the partners in the model HB complex with geometries frozen to match those in the complex. The strain energy in the protonated diamine can be obtained as follows:

$$SE(\mathrm{DAH^+})] = [HB(\mathrm{DAH^+}) + SE(\mathrm{DAH^+})] - HB(\mathrm{DAH^+}) \quad (43)$$

Detailed information of isodesmic reaction and intramolecular hydrogen bond energy calculations can be found from Supporting Information of ref. III.

2.4 Chemicals and Solvents

The origin or synthesis and purification of acids and bases used, is described in detail or references are given in publications I–III. In case of commercially available chemicals the purity was the most important criterion on choosing.

The requirements for the solvent suitable for work I have been described before.[28] The commercial heptane was used (Romil, Super Purity Solvent, assay 99.9%), it was additionally dried before use by letting it stand on molecular sieves (Aldrich, 4 Å, 4–8 mesh) for at least 3 days. The molecular sieves were dried before use by keeping them in vacuo (<1 Torr) and then heating to 300°C in vacuo until the pressure remained constant.

In works II and III, commercial THF (Romil, ≥99.9%) and AN (Romil, ≥99.9%) with water concentration stated by producer below 0.005% were used. The water content of AN determined by coulometric Karl Fischer titration was below 0.004%. THF was distilled from $LiAlH_4$ under argon before using.

The best guarantee of purity during the titrations gives the spectra. If any side-reaction with visible or invisible impurity occurs it would either change the shape of spectra or simply Beer's law would not be valid during the titration. In case of mass-spectrometry, the impurities of bases would also be visible on spectra.

3 EXPANDING THE ACIDITY SCALE OF NEUTRAL BRØNSTED ACIDS IN HEPTANE

3.1 Introduction

Acidity data in solvents of low polarity are very valuable for several reasons, including (1) the possibility to investigate compounds in an environment that has less influence on their properties than do the polar solvents, (2) the possibility to study systems of extraordinarily high or low acidity, and (3) the possibility to mimic real processes in organic synthesis and chemical technology, many of which are carried out in nonpolar media.[28,I]

It is of interest to study acid-base properties of compounds in a medium with dielectric constant around or less than 2 because such a medium is on halfway between the gas phase and polar solvents by the strength of the attractive electrostatic forces between ions. In such a nonpolar medium, ions will not dissociate but will form ion pairs instead. The acidities measured in such a medium are called ion-pair acidities and expressed as pK_{ip} values (see equations 18 and 19). [28,I]

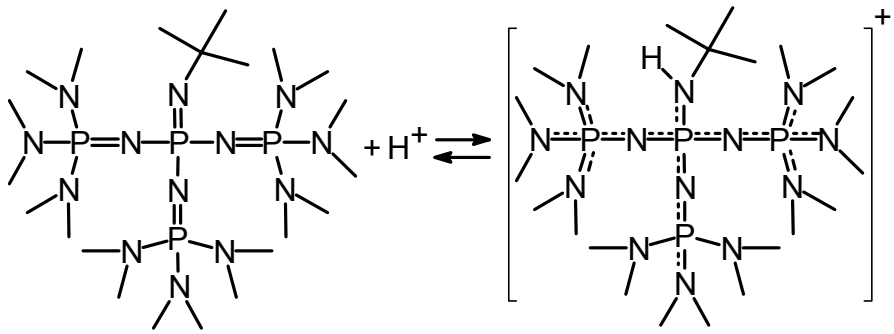
Heptane is a solvent with dielectric constant below 2 (D = 1.92[11]) and very weak solvating power toward polar and especially ionic species. It is easy to dry and purify and it has favourable UV-Vis spectral properties: in theory it is transparent down to well below 190 nm, in practice down to about 210 nm (due to impurities).

The acidity of not all acids can be studied easily in heptane. The acids should as nonpolar as possible and should not have polar centres, such as -OH. To prevent extensive ion aggregation and eventually precipitation of salts in such environment, the anions of the acids should have the following properties: (1) The charge of the ion should be as delocalised as possible, (2) the ion should have no well-defined ionic centres, such as -O^- and (3) the ion should be as large as possible.[28,I]

The base for deprotonation of the acids should be a very strong base, which is soluble in heptane and able to deprotonate acids in nonpolar medium. For a better stability, it should be as large as possible, have a hindered protonation centre and very delocalised charge in ionic form.[28,50,I]

In work I the phosphazene *t*-Bu-P_4(dma) (see Figure 2) — a very strong sterically hindered base — was used as the deprotonating agent. The protonated form of this base — a large cation with very delocalised positive charge — is a good counterion, because specific and electrostatic attraction effects between it and the anions are practically negligible. [28,50,I]

Figure 2. The Structure of the Base *t*-Bu-P_4(dma) and its Protonated Form.



The methods of measurements, calculations and experimental set-up are described in earlier sections (Sections 2.2.4, 2.2.5 and 2.2.6 respectively).

3.2 Results and Discussion

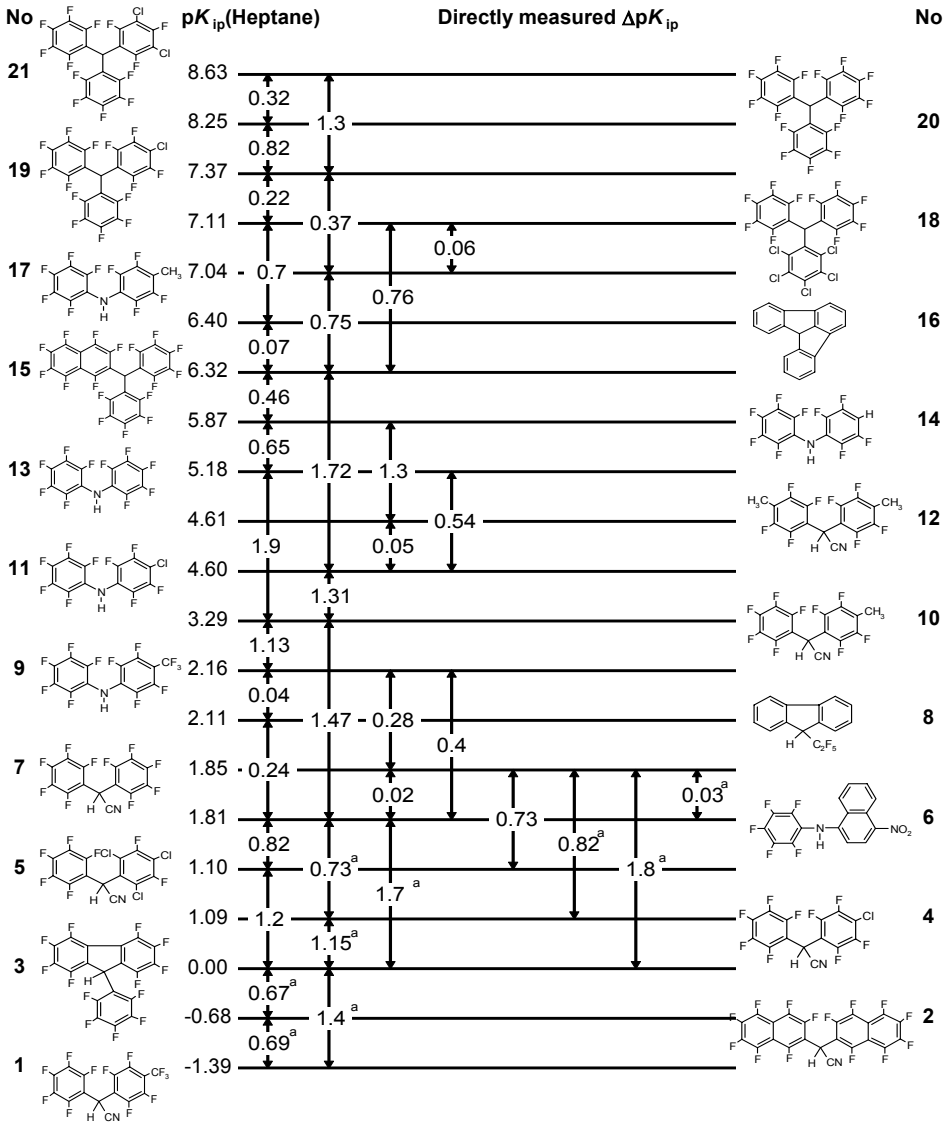
The results of the measurements are presented in Table 2. The acidity scale includes 21 bulky CH and NH acids and spans for about 10 pK_{ip} units.

The compounds as well as their salts with *t*-Bu-P_4(dma) were found to be sufficiently soluble in heptane. The Beer's law was found to hold for the acids and their anions at the low concentrations [$(1 \cdot 10^{-6})$-$(1 \cdot 10^{-4})$ mol/L] used.

Each arrow in Table 2 represents the relative acidity of an acid pair calculated as an average value from the titration points one titration experiment. To make the results more reliable and to be able to estimate the consistency of the results, multiple overlapping measurements were carried out. The entire acidity range from 1 to 21 involves two independent pathways of measurements, and the relative acidity of any two acids can be obtained by combining at least two independent sets of measurements. The uncertainties of the results are best estimated from Table 2 by observing how good the agreement is between different pathways of measurements.

The pK_{ip} values of the individual compounds were obtained using the least squares minimisation procedure described in reference 23. The scale is anchored to an arbitrarily chosen reference compound 3, for which pK_{ip} was arbitrarily taken as 0. For results in work I, the standard deviation of minimisation s = 0.06 pK units.[23] This is a low enough value for the scale to be considered self-consistent. This value was also taken as the basis for giving the absolute pK_{ip} values with two decimal places. Many of the compounds investigated in this work have also been studied in DMSO[51,52,53,54] or 1,2-dimethoxyethane[55,56] (DME) solutions and in the gas phase.[53,54,26,6]

Table 2. Spectrophotometric Acidity Scale in Heptane.



[a] — Measurements from the first paper of this series 28. The scale is anchored to arbitrarily chosen reference compound **3**.

The overall correlation between the acidities in heptane and in the gas phase is presented in Figure 3.[I] The correlation equation* is as follows:

$$\Delta G_{acid} = (308.2 \pm 1.6) + (1.69 \pm 0.33)pK_{ip}(\text{heptane}) \quad (44)$$

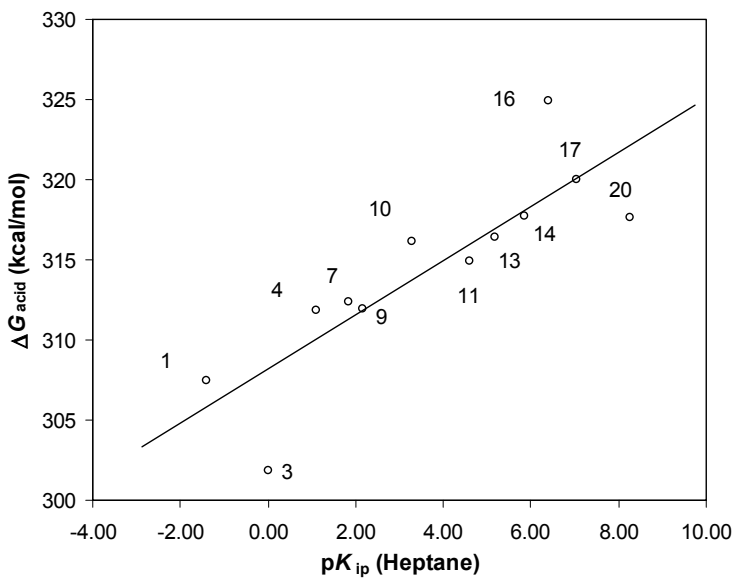
$$r^2 = 0.72,\ s = 3.3 \text{ kcal mol}^{-1},\ n = 12. \quad (45)$$

Although heptane is perhaps one of the most similar solvents to the gas phase, the correlation is poor. The compound that deviates the most from the correlation line is **3** (also **16** and **20** to a lesser extent). The attenuation factor,[57] which reflects the sensitivity of reaction series toward the substituent effects while going from the gas phase into heptane, is:

$$(1000 \cdot 1.69/2.30RT) = 1.24 \quad (46)$$

Therefore, in general, the intrinsic acidities in the gas phase are 1.24 times more sensitive towards substituent effects than in heptane.[I]

Figure 3. Correlation **b**etween the pK_{ip} Values in Heptane and Acidities in the Gas Phase of the Compounds **1**, **3**, **7**, **14**, **20**;[6] **4**, **10**, **16**;[26] **9**;[54] and **11**, **13**, **17**.[53]

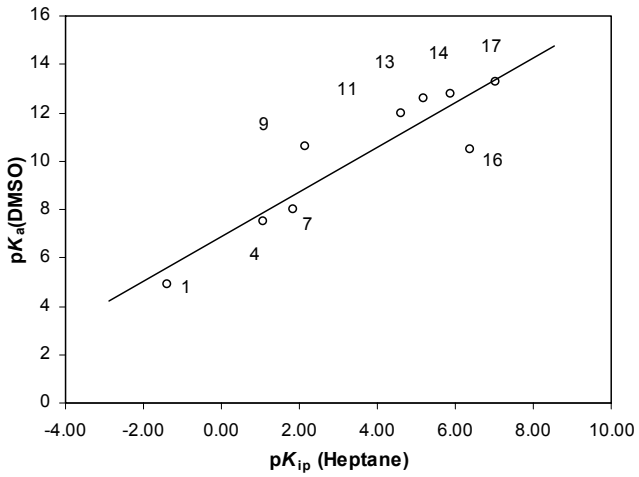


* In all the correlation equations, the standard deviations of the regression coefficients are given as their uncertainties.

Correlations within acid families are significantly better. The correlation of diarylacetonitriles used in this work (**1**, **4**, **7**, **10**) gives the attenuation factor 1.31 (r^2 = 0.98). For NH acids (**9**, **11**, **13**, **14** and **17**) the attenuation factor is 1.21 (r^2 = 0.98).[I]

The overall correlation between the NH and CH acidities in heptane and DMSO is presented in Figure 4.

Figure 4. Correlation Between the pK_{ip} Values in Heptane and DMSO of the Compounds 1, 4;[53] 7, 16;[52] and 9, 11, 13, 14, and 17.[51]



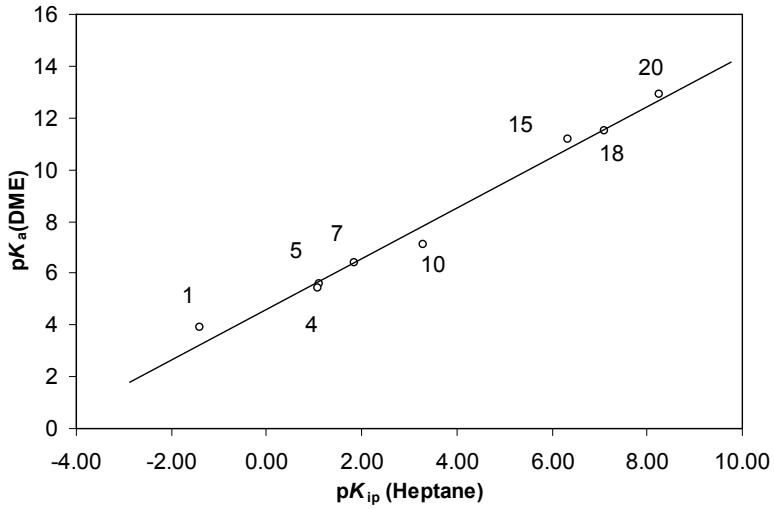
$$\mathrm{p}K_a(\mathrm{DMSO}) = (6.89 \pm 0.71) + (0.92 \pm 0.16)\ \mathrm{p}K_{ip}(\mathrm{heptane}) \qquad (47)$$

$$r^2 = 0.83,\ s = 1.26,\ n = 9. \qquad (48)$$

The slope 0.92 ± 0.16 does not permit one to make any conclusions for the relative differentiating power[11] (which reflects the change of the sensitivity of reaction series toward the substituent effects while going from the DMSO into heptane) of heptane and DMSO. However, for only NH acids (**9**, **11**, **13**, **14**, **17**) the slope would be 0.57 ± 0.04 (r^2 = 0.98) and heptane differentiates these NH acids 1/0.57 = 1.76 times better than DMSO.[I]

The correlation between the acidities in heptane and 1,2-dimethoxyethane (DME) is presented in Figure 5.

Figure 5. Correlation Between the pK_{ip} values in Heptane and 1,2-dimethoxyethane (DME) of the Compounds 1, 4, 7, 10, 15, 18, 20,[56] and 5.[55]



$$pK_{ip}\ (DME) = (4.63 \pm 0.24) + (0.98 \pm 0.05)\ pK_{ip}(heptane) \qquad (49)$$

$$r^2 = 0.98,\ s = 0.45,\ n = 8. \qquad (50)$$

One can see that for the studied group of CH acids the differentiating power of heptane does not differ significantly from that of DMSO or DME. This does not hold for the studied group of NH acids: heptane appears to be 1.76 times better differentiator for these acids than DMSO.[I]

It was demonstrated earlier[52,53,26] that the solvent attenuation factors depend significantly on the nature of the deprotonation centre of the acids (CH, NH, OH, etc.) as well as on the given collection of included substituents. Therefore, a significantly more extensive data bank of pK_{ip} values in heptane is needed to further study of the relative differentiating power of the gas phase, apolar and dipolar aprotic solvents of Brønsted acids of different classes.

As a demonstration of the influence of substituent effects, the acidity order of compounds **19**, **20** and **21** will be discussed here. In the anion of compound **19** the chlorine in the *para* position of the tetrafluorinated phenyl group has a resonance acceptor effect in the interaction with the carbanion center. This effect is absent in compound **20** making it by 0.9 ΔpK_{ip} units weaker compared to **19**. In the compound **21** the induction acceptor effect of the *meta* chlorine atoms is weaker than that of the *meta* fluorine atoms in **20**. The resonance acceptor effect is irrelevant in the *meta* position and hence compound **21** is approximately 0.4 ΔpK_{ip} units weaker than **20**.

3.3 Conclusions

The results in work I demonstrate that experimental studies of acid-base equilibria can be readily carried out, even in solvents of polarity as low as heptane. The success of the experiments is, however, critically dependent on the base used for deprotonation of acids (the protonated form of the base must be bulky and have very extensively delocalised charge) as well as on the choice of acids (their anions must have as delocalised charge as possible).

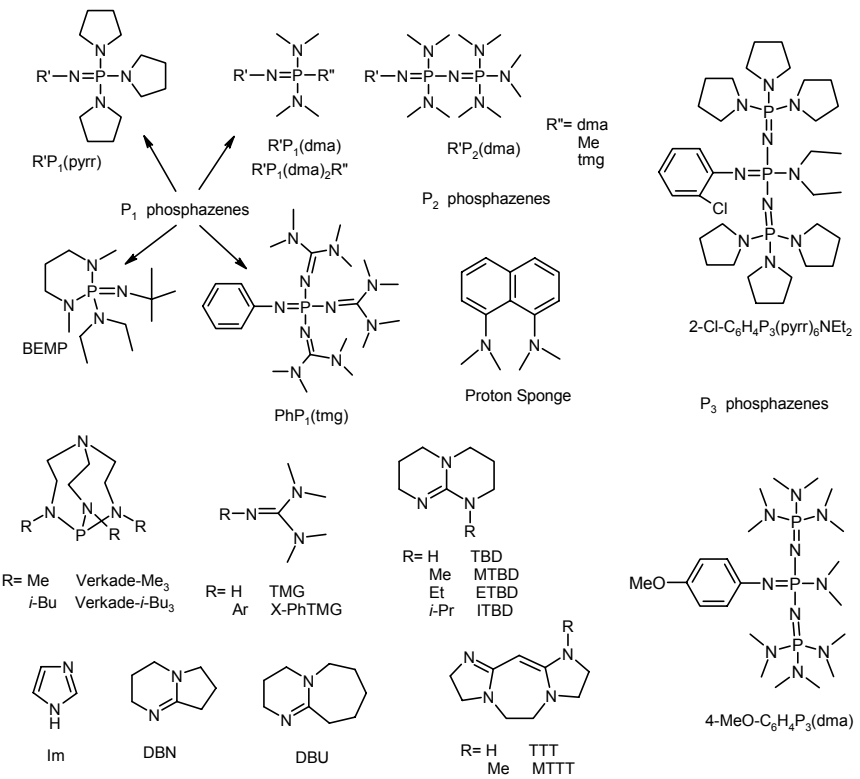
The UV-vis spectrophotometric ion-pair acidity scale in heptane includes now 21 bulky CH and NH acids and spans for about 10 orders of magnitude. It was demonstrated that the substituent effects on the acidity of the studied CH acids are attenuated by ca 1.2 times when the gas phase is substituted for heptane. In its turn, for the series of NH acids, the latter is found to be a more differentiating solvent than DMSO.

4 EXPERIMENTAL GAS-PHASE BASICITY SCALE OF SUPERBASIC PHOSPHAZENES

4.1 Introduction

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.[58] However, the practical success in realization of this promise has been very limited to date. Acoording to work II there have been only two works reporting experimental gas-phase basicity data for phosphazene bases, [59,17] 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 vapour 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".

Figure 6. Structures of Compounds Measured in this Work or Used in Discussion.



In work II it was possible to overcome both of these complications and as a result a continuous phosphazene-based gas-phase basicity ladder with the span of ca 20 kcal·mol^{-1} from which around 15 kcal·mol^{-1} is an extension of the so far existing continuous gas-phase basicity scale of organic bases was presented.

4.2 Results

Gas-Phase Basicity Measurements. In addition to previously[17] 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 17 these form the extension of the so far existing[59,33] experimental self-consistent gas-phase basicity scale towards the region of higher basicity of organic bases. MTBD was chosen as the anchor compound for the present scale as its published *GB* value (*GB* = 246.2 kcal·mol^{-1})[33] 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 3.

Gas-Phase Basicity Calculations. The results of calculation of the basicities of the phosphazene superbases described in this work are summarized in Table 3. Detailed results of the calculations and the Cartesian coordinates of the calculated species are available in the Supporting Information of work II.

4.3 Discussion

Extension of the experimental gas-phase basicity scale. The results of this work have extended the gas-phase basicity scale of organic compounds to *GB* = 264.6 kcal·mol^{-1}. 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.

There are now available experimental *GB* values for two homological series of phosphazenes — for the pair **24** and **2** and for and pair **29** and **4**. The base strengthening effects in the homological rows, when going from arylsubstituted P_1 to P_2 phosphazenes are 15.6 and 16.8 kcal·mol^{-1}, respectively. This gives a direct experimental support for the earlier suggestions of theoretical works[9,18] to use homological series of phosphazenes to further extend the basicity scale in the gas phase.

Table 3. Experimental and Calculated Gas-Phase Basicities of the Studied Bases and Reference Values from Different Media.

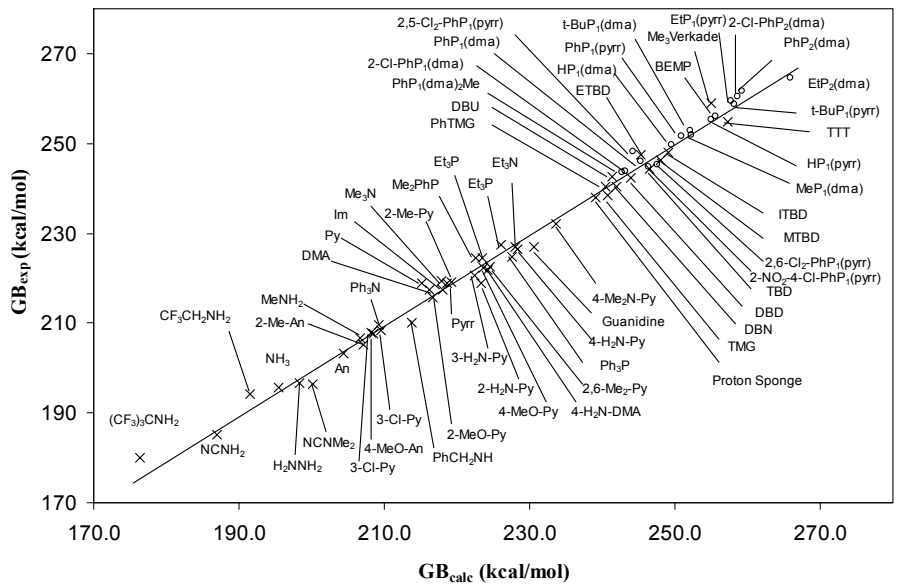
No	Base	Directly measured $\Delta\Delta G_b$ [a]	GB_{exp} [b]	GB_{calc} [c]	pK_a(AN) [d]	pK_{ip}(THF) [e]	pK_a(THF) [e]	$pK_a(H_2O)$ [f]
1	EtP_2(dma)		264.6	265.9	32.94 [g]	24.9	25.3	
2	PhP_2(dma)		261.7	259.2 [h]	26.46	19.4	19.8	
3	Verkade-iBu_3		260.8		33.58 [i]			
4	2-Cl-$C_6H_4P_2$(dma)		260.5	258.7	24.23 [h]	15.8 [h]	16.3 [j]	
5	EtP_1(pyrr)		259.6	257.8	28.88	21.7	21.7	
6	Verkade-Me_3		259.1	255.0	32.90 [i]			
7	t-BuP_1(pyrr)		258.7	258.2	28.42	20.2	20.2	
8	4-Me_2N-$C_6H_4P_1$(pyrr)		257.5		23.88	17.3	17.3	12.00
9	BEMP		256.0	255.6	27.63 [k]	19.3 [j]	19.0 [j]	
10	HP_1(pyrr)		255.2	255.0 [h]	27.01	20.8	20.8	
11	4-MeO-$C_6H_4P_1$(pyrr)		254.9		23.12	16.8	16.8	11.94
12	t-$OctP_1$(dma)		254.2		26.49 [k]	18.5	18.5	
13	t-BuP_1(dma)		252.9	252.1	26.98	18.9 [j]	18.9 [j]	
14	MeP_1(dma)		251.9	252.3 [l]	27.52	20.7	20.7	
15	PhP_1(pyrr)		251.7	250.9	22.34	16.1	16.1	11.52
16	1-NaphthtP_1(pyrr)		250.9		20.61	14.2 [m]	14.2 [m]	
17	2-Cl-$C_6H_4P_1$(pyrr)		250.8		20.17	13.2 [m]	13.2 [m]	9.98
18	HP_1(dma)		249.6	249.2 [l]	25.85	19.7	19.7	
19	4-Br-$C_6H_4P_1$(pyrr)		249.3		21.19	15.4 [m]	15.4 [m]	11.23
20	2,5-Cl_2-$C_6H_3P_1$(pyrr)		248.2	244.2	18.52	11.9 [m]	11.9 [m]	9.21
21	ITBD		247.9	249.1				
22	ETBD		247.5	245.3				
23	MTBD [j]		246.2 [n]	248.0	25.44 [k]	18.6	18.6	
24	PhP_1(dma)		246.1	245.3 [h]	21.25	15.2 [m]	15.2 [m]	10.64
25	2-NO_2-5-Cl-$C_6H_3P_1$(pyrr)		245.8		17.27	10.1 [m]	10.1 [m]	8.33
26	4-CF_3-$C_6H_4P_1$(pyrr)		245.4		20.16	14.6 [m]	14.6 [m]	10.65
27	2,6-Cl_2-$C_6H_3P_1$(pyrr)		245.3	247.5	18.56	11.8 [m]	11.8 [m]	9.00
28	2-NO_2-4-Cl-$C_6H_3P_1$(pyrr)		244.9	246.4	17.68	10.8 [m]	10.8 [m]	8.37
29	2-Cl-$C_6H_4P_1$(dma)		243.7	243.2	19.07	12.5 [m]	12.5 [m]	
30	PhP_1(dma)$_2$Me		243.7	242.7	21.03	15.4	15.4	

[a] Directly measured experimental $\Delta\Delta G_b$ (kcal·mol^{-1}) values obtained from FT-ICR measurements. [b] Estimated absolute *GB* (kcal·mol^{-1}) values for bases. 1 kcal·mol^{-1}= 4.184 kJ/mol. [c] Results of basicity calculations at DFT B3LYP/6–311+G** level (kcal·mol^{-1}), this work if not noted otherwise. [d] Reference 25 if not noted otherwise. [e] Reference 17. [f] Reference 60. [g] Reference 50. [h] Reference 18. [i] Reference 61. [j] Present work. [k] Reference 62. [l] Reference 9. [m] Reference 16. [n] anchor of the scale, *GB* value taken from ref 33.

Correlation of GB_{exp} with GB_{calc}. It is of great interest to compare the experimentally measured and calculated at DFT B3LYP/6–311+G** level *GB* values of the compounds studied in the present work. The overall correlation of available data above 176 kcal·mol^{-1} presented in Table 3 gives the following equation: $GB_{exp} = 1.01\ GB_{calc} - 2.36$ the standard deviations of the slope and intercept are 0.01 and 2.77, respectively, $R^2 = 0.992$; $n = 63$ and $s = 2.0$ kcal·mol^{-1}. For phosphazene bases only the correlation is similar: $GB_{exp} = 0.99\ GB_{calc} + 2.67$, the standard deviations of the slope and intercept are 0.06 and 14.68, respectively, $R^2 = 0.951$; $n = 17$ and $s = 1.6$ kcal·mol^{-1}. 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 the ICR experiments) and calculations

(high demand of calculation power, danger to stop at local energy minima etc.). These two correlations are in agreement with previous findings[48] that *GB* values for neutral bases calculated at DFT B3LYP/6–311+G** level are of comparable quality with experimental measurements. The standard deviation (2.0 kcal·mol^{-1}) of overall correlation observed in this work for *GB* range 176 to 265 kcal·mol^{-1} is similar to the standard deviation (1.8 kcal·mol^{-1}) observed in the previous work[48] for the *GB* range from 35 to 278 kcal/mol of various bases.

Figure 7. 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.

Influence of the imino-substituent on the gas-phase basicity of P_1-phosphazenes. In the families of both P_1(dma) and P_1(pyrr) phosphazenes the basicity increases in the row Ph < H < *t*-Bu < Et (in the case of P_1(pyrr) the last is not investigated). The interesting feature of this basicity order is Ph < H.

Attaching a phenyl ring to the basicity centre instead of a hydrogen atom has both basicity-enhancing and -decreasing effects: (1) the increase of polarizability in ionic forms increases the basicity and (2) the increased resonance in the neutral base (in those cases where this is possible) and the slight induction-acceptor decrease the basicity. In addition, in solution the attached phenyl ring causes considerable steric hindrance to solvation or the protonated form.

In the gas phase, attaching a phenyl ring to the basicity centre of the ammonia or tetramethylguanidine (TMG) leads to basicity increase while in the case of the phosphazene bases the effect of the phenyl ring is basicity-decreasing. In ammonia and TMG the change of polarizability in ionic forms is the dominating factor and increases the basicity. In the case of phosphazenes the molecules of the neutral bases are ylide-like: the P=N fragment has a strong P^{+}–N^{-} character. Therefore the resonance effect of the basicity centre with the phenyl ring in the neutral molecule is very strong. On protonation this effect is lost. Additionally the basicity is decreased by the steric hindrance that is invoked on protonation. These two factors are more powerful than the increased polarizability and basicity decrease is observed on introduction of the phenyl ring.

In solution a phenyl ring attached to the basicity centre invariably leads to basicity decrease because the polarizability effect is not operational and the bulky substituent hinders stabilisation of the protonated form by solvation.

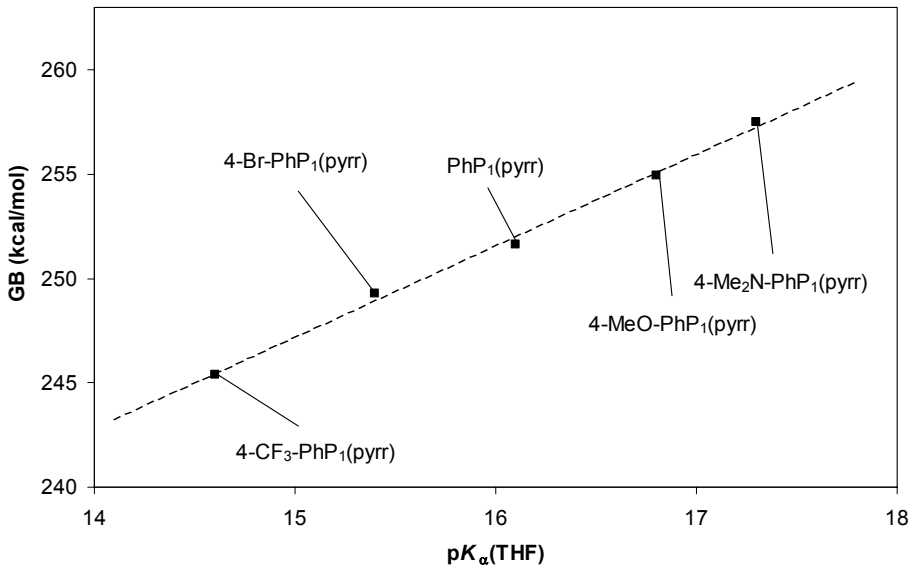
Correlations of GB_{exp} with solution basicities. Additional discussion of the relationship of gas-phase and solvent basicities can be found in the Supporting Information of work II. The solvent influence on compounds basicity is obtained by correlating basicity values in the gas-phase and solvent. The correlation equation has the following form:

$$GB(\text{kcal/mol}) = a\ \text{p}K(\text{X}) + b, \qquad (51)$$

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

As an example of correlations between GP and THF, for 4-substituted PhP_1(pyrr) series (where access of the solvent molecule into the protonation centre is not affected by the substituents in the phenyl ring) the correlation is excellent (R^2 = 0.996). For this series the gas phase is 3.20 times better differentiating medium of basicities than THF (see SI of ref. II for details). It can be concluded that for the PhP_1(pyrr) series moderate variation of the molecule size (or volume) H vs. MeO or Me_2N in the periphery relative to the protonation centre does not have substantial influence on the size, as it can be understood in terms of size-enhanced cation stabilisation ability in the gas-phase.

Figure 8. Correlation Between 4-substituted PhP_1(pyrr) Series in THF and GP.



4.4 Conclusions

The results of this work have extended the continuous gas-phase basicity scale of organic compounds further to *GB* = 264.6 kcal·mol^{-1}. 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.

5 BRØNSTED BASICITIES OF DIAMINES IN DIFFERENT MEDIA

5.1 Introduction

Due to the high importance and wide usage of diamines, their design and basicity both in the gas phase[49,63–70] and liquid phase[38,67–71] has been the topic of a number of reports and a review.[72] It is well known that the enhanced basicity of diamines in the gas phase with respect to similar monoamines is caused by the intramolecular hydrogen bond[63,64] and that in the condensed phase this effect can be lower or absent, depending on the solvent and on the accessibility of the protonated amine for solvent molecules.[72,73] The energetic effect of hydrogen bond formation on basicity has been the subject of studies on several types of diamines: α,ω-alkanediamines,[63,64] bicyclic amines and diamines,[66] proton sponges,[49] bispidines,[69] etc. The situation is, however, more complicated and the formation of intramolecular hydrogen bond cannot be regarded as a standalone process. It is instead coupled with strain effects[72] and it is desirable to estimate the effect of different contributing factors separately. Howard[49] has summarized the factors that are responsible for determining the eventual basicity of a diamine: (1) The effective proton affinity of one of the amino groups; (2) the stabilization effect caused by formation of the intramolecular hydrogen bond in the cation; (3) the relief of steric strain on protonation by loss of repulsion between lone pairs of electrons in the neutral; (4) introduction of steric strain by "folding" of the diamine molecule during the formation of intramolecular hydrogen bond; (5) the difference in solvation energies of the neutral and the protonated form.

The basicity of the simplest class of diamines — α,ω-alkanediamines — and their alkyl-substituted derivatives has been the topic of numerous reports.[63–65,73–75] However, no systematic studies aiming at insight into the origin of their basicity (similar to ref 49) and involving a wide structural variety of compounds have been reported.

This part of the thesis attempts to fill the abovementioned gaps by providing a comprehensive basicity study of α,ω-alkanediamines, their alkylated derivatives (Figure 9) and some related bases (Figure 10). Both experiment and computations are presented. As a result basicities were measured for 16, 14 and 9 diamine bases in AN, THF and GP, respectively. In addition the gas-phase basicities and equilibrium geometries were computed for 19 diamino bases and 15 related monoamines at DFT B3LYP 6–311+G** level. The effects of the different factors (intrinsic basicity of the amino groups, formation of intramolecular hydrogen bond and molecular strain, see above) determining diamine basicities were estimated for a number of α,ω-alkanediamines and related bases using the method of isodesmic reactions.

Figure 9. Diamines Studied in this Work.

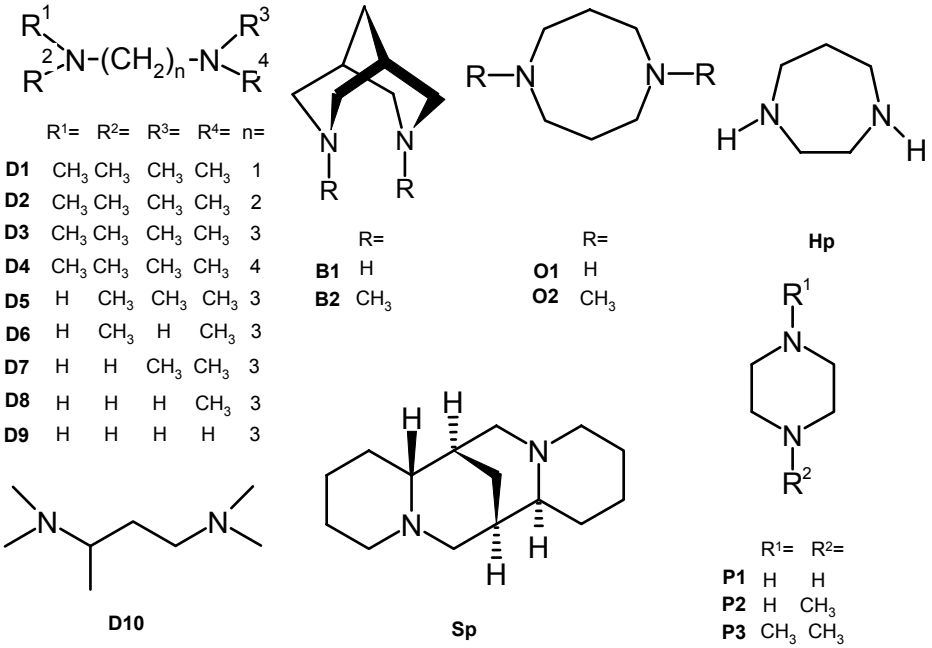
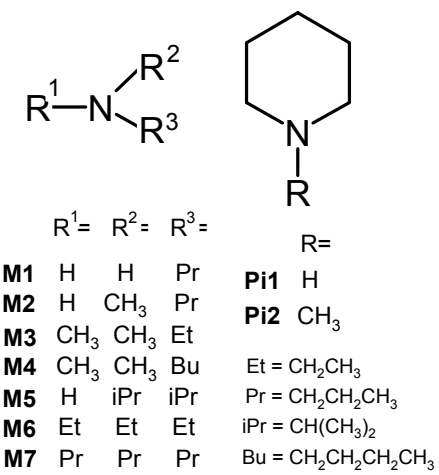


Figure 10. Studied Monoamines Related to the Diamines in this Work.



5.2 Results

The results of basicity measurements and calculations are presented in Table 4.

Table 4. Results of Experimental Basicity Determinations in the Gas Phase, AN, THF and Calculations in the Gas Phase.[a]

Base	pK_a(AN)	pK_{ip}(THF)	pK_α(THF)	pK_a(H_2O)	GB_{exp}[b]	GB_{calc}
			Diamines			
D1	–	–	–	7.67[c]	–	226.3
D2	18.68	13.4	12.8	9.15[c]	230.5, 232.0[d]	231.2
D3	19.27	13.6	13.0	10.6[c]	235.2, 235.5[d]	234.8
D4	19.93	13.4	13.1	10.80[c]	237.3[d]	236.4
D5	20.01	14.9	14.3	–	233.3	234.7
N,N'-Dimethyl-ethanediamine	19.63[c]	–	–	10.1[c]	226.3[d]	–
D6	20.39	15.5	14.9	–	–	231.2
D7	19.57	15.3	14.7	9.75[c]	231.9, 233.1[d]	234.2
D8	20.04	15.8	15.2	–	227.3	231.4
1,2-ethanediamine	18.46[e]	–	–	10.1[c]	218.1[d]	–
D9	19.70, 19.70[e]	–	–	10.6[c]	224.7[d]	226.9
1,4-butanediamine	20.12[e]	–	–	10.72[c]	228.1[d]	–
D10	20.09	14.1	13.4	–	237.9	236.7
B1	21.55	–	–	–	–	232.7
B2	22.74	15.5	15.4	9.38[f]	240.8	238.5
Sp	21.66[g]	14.2	14.3	11.96[f], 12.11[c]	243.4	240.8
Hp	19.10	15.1	14.4	10.41[f]	223.6	225.0
P1	18.69	14.9	14.2	9.7[c]	218.6[d]	218.8
P2	18.07	14.1	13.4	9.32[c]	–	223.0
P3	17.36	13.1	12.4	8.54[c]	–	227.2
			Monoamines			
M1	18.43, 18.22[e]	14.7	13.8	10.7[c]	211.3[d]	211.8
M2	18.92	14.6	13.7	–	–	218.2
N,N-Dimethyl-propylamine	18.3[h]	13.5[h]	12.7[h]	10.16[f]	222.7[d]	221.2
M3	18.33	13.6	12.6	10.16[f]	222.1[d]	221.4
M4	18.24	13.4	12.8	10.19[f], 10.65[c]	224.2[d]	222.8
M5	18.81	14.6	13.6	11.2[c]	222.9, 224.3[d]	222.1
M6	18.82[i]	14.0[j]	12.5[j]	10.7[c]	226.1, 227.0[d]	228.2
M7	18.25, 18.10[e]	13.1	13.0	10.7[c]	229.5[b]	229.0
Pi1	19.29, 18.92[e]	15.0	14.3	11.1[c]	220.0[d]	220.4
Pi2	18.25, 18.01[k]	13.6	12.9	10.1[c]	224.7[d]	224.0

Base	pK_a(AN)	pK_{ip}(THF)	pK_α(THF)	pK_a(H_2O)	GB_{exp}[b]	GB_{calc}
Various Other Bases						
Aniline	10.62[i]	7.0[j]	5.2[j]	4.6[f]	203.3[d]	204.4[j]
N,N-dimethylaniline	11.43[i]	6.5[j]	4.9[j]	5.1[f]	217.3[d]	216.2[j]
Pyridine	12.53[i]	7.4[j]	5.5[j]	5.3[f]	214.7[d]	215.2[j]
Guanidine	–	–	–	13.6[c]	226.9[d]	230.6[j]
TMG	23.3[j]	17.0[j]	15.5[j]	13.6[f]	238.4[d]	240.7[j]
PhTMG	20.84[i]	15.0[j]	14.0[j]	11.77[l]	240.4[d]	240.5[j]
DBU	24.34[i]	18.1[j]	16.9[j]	–	242.7[d]	241.3[j]
TBD	26.03[i]	21.7[j]	21.0[j]	–	244.3[d]	246.5[j]
MTBD	25.44[i]	18.6[j]	18.6[j]	–	246.2[d]	248.0[j]
HP_1(pyrr)	27.01[i]	20.8[j]	20.8[j]	13.9[m]	255.2[j]	255.0[j]
tBuP_1(pyrr)	28.42[i]	20.2[j]	20.2[j]	–	258.7[j]	258.2[j]
PhP_1(pyrr)	22.34[i]	16.0[j]	16.0[j]	11.52[l]	251.7[j]	250.9[j]
HP_1(dma)	25.85[i]	19.7[j]	19.7[j]	13.3[m]	249.6[j]	249.9[j]
tBuP_1(dma)	26.98[i]	18.9[j]	18.9[j]	–	252.9[j]	252.1[j]
PhP_1(dma)	21.25[i]	15.3[j]	15.3[j]	10.64[l]	246.1[j]	245.3[j]
HP_1(tmg)	–	27.9[j]	28.6[j]	–	–	276.1[j]
PhP_1(tmg)	31.4[j]	23.7[j]	24.3[j]	–	–	274.0[j]
PhP_2(pyrr)	27.55[i]	20.2[j]	20.9[j]	–	–	–
EtP_2(dma)	32.94[n]	24.9[j]	25.3[j]	–	264.6[j]	265.9[j]
PhP_2(dma)	26.46[i]	19.4[j]	19.9[j]	–	261.7[j]	259.2[j]
Verkade's Base	32.9[o]	–	–	–	259.1[j]	255.0[j]

a — Values from this work if not indicated otherwise. The data for various other bases have been added for reference. For structures of bases see Schemes S1 and S3 in Supporting Information. *b* — The new measured gas-phase *GB* values (in kcal·mol^{-1}) are anchored to Tripropylamine (**M7**) *GB* value taken from ref 33. *c* — Palm Ed.[12] *d* — Hunter et al.[33] *e* — Coetzee et al.[38] *f* — Perrin Ed.[13]. *g* — Toom et al.[76] *h* — Estimated as the average of measured basicities of M3 and M4. *i* — Kaljurand et al.[25] *j* — Most recent value from Rodima et al[16] or Kaljurand et al[17,II] or Kolomeitsev et al.[18]. *k* — Pawlak et al.[77] *l* — Sooväli et al.[60] *m* — Estimated values from Sooväli et al.[60] *n* — Schwesinger et al.[50] *o* — Kisanga et al.[61]

Full results of basicity measurements in THF, AN and both measurements and calculations in the gas phase are available in work III, Tables S2, S3, S4 and S5 of its Supporting Information (SI).

Basicity measurements in AN. The absolute pK_a values were calculated as in the previous papers[24,25] by minimizing the sum of squares of differences between directly measured ΔpK_a values and assigned pK_a values while keeping the pK_a values of reference bases (taken from ref 25) constant. It should be stressed, that the absolute pK_a values of bases given in Table 4 are not as accurate as the relative pK_a values. The consistency of the results can be assessed using a consistency criterion *s* as defined by Equation 8 of ref 24. For

results of work III the s value is 0.04 pK_a units (n_m=58, n_c=23). See the SI of reference III for more details.

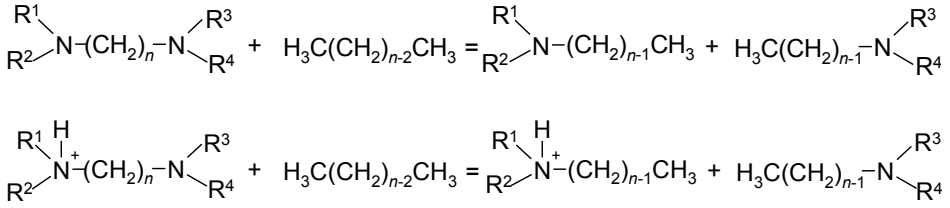
Basicity measurements in THF. The basicity values of the bases were obtained using the same approach as described above for AN. The consistency of the ΔpK_{ip} and ΔpK_α values in THF (only the measurements of this work involved) is similar to previous results[17] that is s = 0.08 (n_m=47, n_c=22). The pK_α values of compounds **D9** and **B1** could not be measured in THF. For **D9** the reason was low solubility of the acid-base complex. For **B1** the p$K_{\alpha1}$ and p$K_{\alpha2}$ values were too close for used measurement method.

Basicity measurements in the gas phase. There are several compounds on the basicity ladder (see Table S4 in SI of ref. III) with published *GB* values.[33] Tripropylamine **M7** was chosen as the anchoring point for the results of this work for the following reasons. (1) There is an excellent agreement between the *GB* value 243.9 kcal·mol^{-1} of **R13** ($PhP_1(dma)_2Me$) measured with **M7** as the anchor point (see the SI) and the *GB* value 243.7 kcal·mol^{-1} of the same compound measured with MTBD (7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene) as the anchor compound in ref II. This means that the present *GB* values are consistent with *GB* values of many other bases over the range 229.5 to at least 264 kcal·mol^{-1}. (2) Doing so the best agreement between measured and calculated *GB* values for the compounds of the present work is observed.

Gas-Phase basicity calculations. The average difference between the calculated and experimental results is 0.1 kcal·mol^{-1} indicating that there is no systematic under- or overestimation of basicity. It is important to note that all qualitative conclusions drawn in the discussion below remain valid, irrespective whether computational or experimental data are used. See the SI of ref. III for more details.

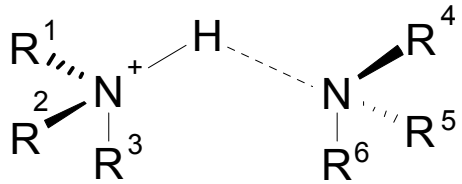
Factors determining the basicity of diamines. In work III the above-mentioned factors (1) to (4) (see 5.1) were quantified using the approach based on isodesmic reactions similarly to that described in ref 49. The isodesmic reactions ID1 to ID16 were used (see Figure 11 as an example and article III for all reactions). The substituents –R^x which are not described here are given in Figure 9. The model systems used for estimating intramolecular hydrogen bond (HB) energies are given in Figure 12. The results of the treatment are presented in Table 5. Full details are given in Tables S6 and S7 in the SI of ref. III.

Figure 11. Example of Isodesmic Reactions.



These two reactions are for bases D2-D9 and for their protonated forms respectively. For R^1 to R^4 see Figure 9.

Figure 12. Model Systems for Estimating Hydrogen Bond Energies.



	>N$^+$-				>N-	
	R^1	**R^2**	**R^3**	**R^4**	**R^5**	**R^6**
a	-CH_3	-CH_3	-H	-CH_3	-CH_3	-H
b	-CH_3	-CH_3	-H	-CH_3	-CH_3	-CH_3
c	-CH_3	-CH_3	-CH_3	-CH_3	-CH_3	-H
d	-CH_3	-CH_3	-CH_3	-CH_3	-CH_3	-CH_3
e	-CH_3	-H	-H	-CH_3	-H	-H
f	-CH_3	-H	-H	-H	-H	-H
g	-CH_3	-CH_3	-H	-CH_3	-H	-H
h	-CH_3	-CH_3	-H	-H	-H	-H
i	-H	-H	-H	-H	-H	-H
j	Pr	-H	-H	Pr	-H	-H

Table 5. Results of the Analysis of Diamine Basicity Using the Isodesmic Reactions Approach.[a]

Com-pound	*PA*(DA)[b] kcal mol^{-1}	*PA*(MA)[b] kcal·mol^{-1}	*PA*(DA)-*PA*(MA) kcal·mol^{-1}	*SE*(DA)[c] kcal·mol^{-1}	[*HB*(DAH$^+$)+*SE*(DAH$^+$)][d] kcal·mol^{-1}	[*H*(DAH$^+_{HB}$)-*H*(DAH$^+_{NHB}$)][e] kcal·mol^{-1}	*HB*(DAH$^+$)[f] kcal·mol^{-1}	*SE*(DAH$^+$)[g] kcal·mol^{-1}	Length of *HB*(DAH$^+$)[h] Å	α(N$^+$H···N)[i] deg
D1[j]	234.0	225.8	8.2	–2.3	–10.5		49.9	–60.4	2.57	72.1
D2	240.1	228.8	11.3	2.6	–8.7	–8.9	–10.9	2.2	1.93	125.8
D3	244.0	229.8	14.2	0.4	–13.8	–13.5	–21.0	7.2	1.73	153.6
D4	246.5	230.4	16.1	–0.1	–16.1	–17.2	–25.2	9.1	1.64	170.5
D3	244.0	229.8	14.2	0.4	–13.8	–13.5	–21.0	7.2	1.73	153.6
D5	243.8	229.8 225.9	14.0	0.4	–13.6	–13.7	–20.3	6.7	1.79	150.1
D6	240.4	225.9	14.6	0.2	–14.4	–14.5	–23.1	8.8	1.71	150.9
D7	243.4	219.5 229.8	13.6	0.2	–13.4	–13.3	–18.7	5.3	1.79	150.1
D8	240.6	225.9 219.5	14.7	0.4	–14.2	–14.2	–20.7	6.4	1.76	148.2
D9	236.1	219.5	16.6	0.4	–16.2	–16.1	–24.7	8.6	1.68	149.4
D10	246.0	229.8 230.5	15.5	–2.0	–17.5	– 14.2	–21.1	3.6	1.72	155.6
B1[k]	240.7	228.0	12.7	2.3	–10.4		–17.2	6.8	1.84	130.1
B1[l]	240.7	227.5	13.2	2.3	–10.9		–17.2	6.4	1.84	130.1
B2[k]	246.7	231.5	15.2	5.3	–10.0		–17.2	7.2	1.83	134.4
B2[l]	246.7	231.4	15.3	–1.7	–17.1		–17.2	0.1	1.83	134.4
Sp	249.2	236.1	13.1	7.5	–5.6		–16.5	10.8	1.88	132.7
Hp	233.2	227.5 228.6	4.6	6.5	1.9	–4.5	–7.1	9.0	1.96	110.7
P1[m]	226.0	227.5	–1.5	2.3	3.8	2.1	0	3.8	2.34	85.9
P1[n]	223.9	227.5	–3.6	2.3	5.9	2.1	0	5.9	2.34	85.9
P2[m]	230.5	231.4 227.5	–0.9	–2.7	–1.8	4.5	0	–1.8	2.29	90.2
P2[n]	226.0	231.4 227.5	–5.3	–2.7	2.6	4.5	0	2.6	2.29	90.2

Com-pound	*PA*(DA)[b] kcal mol^{-1}	*PA*(MA)[b] kcal·mol^{-1}	*PA*(DA)-*PA*(MA) kcal·mol^{-1}	*SE*(DA)[c] kcal·mol^{-1}	[*HB*(DAH$^+$)+*SE*(DAH$^+$)][d] kcal·mol^{-1}	[*H*(DAH$^+_{HB}$)-*H*(DAH$^+_{NHB}$)][e] kcal·mol^{-1}	*HB*(DAH$^+$)[f] kcal·mol^{-1}	*SE*(DAH$^+$)[g] kcal·mol^{-1}	Length of *HB*(DAH$^+$)[h] Å	α(N$^+$H···N)[i] deg
P3[m]	234.8	231.4	3.4	2.1	–1.3	0.4	–0.2	–1.1	2.32	90.4
P3[n]	234.4	231.4	3.0	2.1	–0.9	0.4	–0.2	–0.7	2.32	90.4
O1[o]	239.3	228.6	10.8	8.7	–2.1		–18.1	16.1	1.74	134.2
O1[p]	239.3	229.1	10.3	1.0	–9.3		–18.1	8.8	1.74	134.2
O2	245.6	232.5	13.1	7.2	–6.0	–11.2	–18.1	12.1	1.73	138.6

a — The structures of the compounds are given in Figure 9. The values in the Table are the values form Equations: *b* – 1 and 2 *c* – 40, *d* – 41, *f* – 42, *g* – 43. The full Table with exact reactions for each compound, computational values of compounds and complexes shown in Figure 12 is given in Ref. III Supporting Information Table S6. *e* — The enthalpy difference between the non-hydrogen-bonded *H*(DAH$^+_{NHB}$) and hydrogen-bonded *H*(DAH$^+_{HB}$) conformers of the protonated diamine (which at the same time is the *PA* difference involving these conformers) is denoted as [*H*(DAH$^+_{HB}$)-*H*(DAH$^+_{NHB}$)]. *h* — The length of the intramolecular HB in protonated diamine. *i* — The angle between nitrogen atoms and hydrogen of hydrogen bond. *j* — The isodesmic reaction data of **D1** are in part meaningless and are given here to be used only in the discussion of the isodesmic reaction approach. *k* — Isodesmic reactions ID11 and ID12. These are considered more justified than reactions ID13 and ID14 and are used in discussion. *l* Isodesmic reactions ID13 and ID14. *m* — Chair conformation. *n* — Boat conformation. *o* — Isodesmic reactions ID7 and ID8. These reactions are considered more justified than reactions ID9 and ID10 and are used in the discussion. *p* — Isodesmic reactions ID9 and ID10

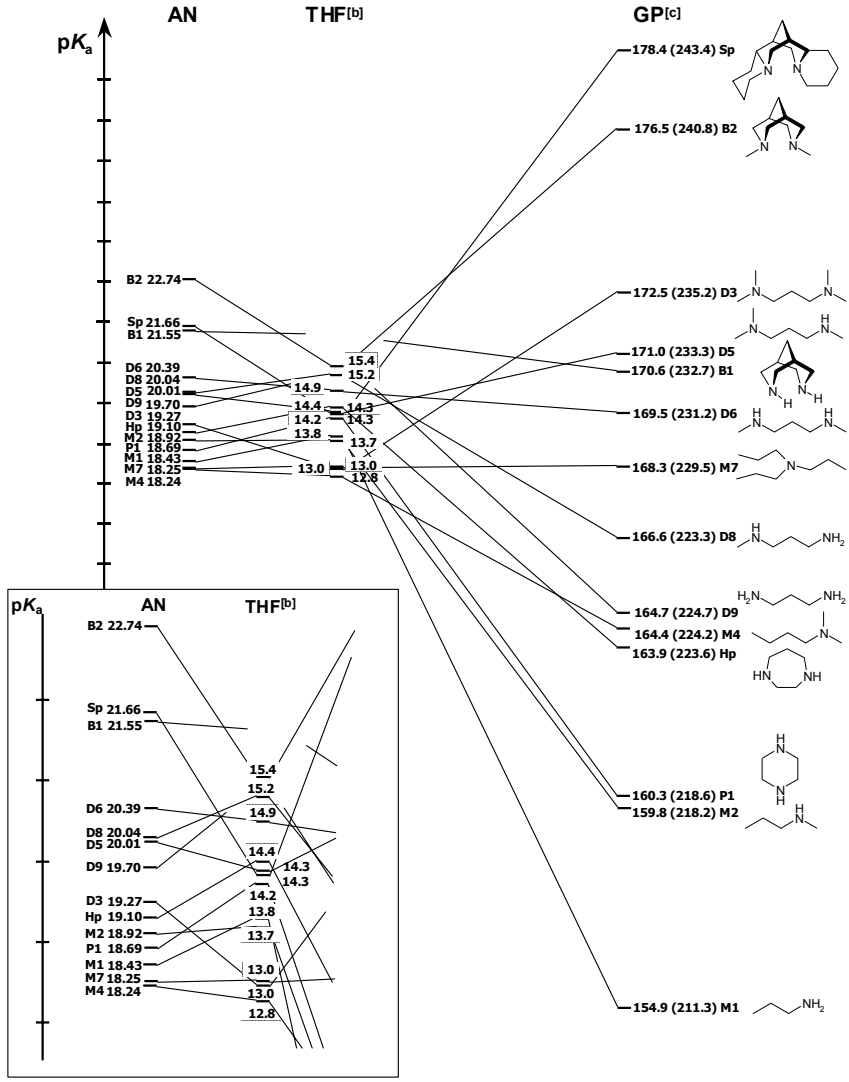
5.3 Discussion

Basicities of 1,3-propanediamines D3-D9. Basicity changes in the row of substituted 1,3-propanediamines (and some other bases) in different media are illustrated in Figure 13.

The basicity of the 1,3-propanediamines in the gas phase increases rather monotonously with increasing level of methylation. This is easily rationalized based on the increase of molecular size and polarizability as well as the electron-donating nature of the methyl substituents.[71] Computational results indicate that in all studied 1,3-propanediamines protonation occurs at the most methylated nitrogen and that the protonated forms of all 1,3-propanediamines are cyclic due to intramolecular hydrogen bond (HB). The diamines are clearly stronger than monoamines of similar size and substitution pattern by ca 9 to 15 kcal·mol^{-1}. Computations using the isodesmic reactions (see Table 5) indicate that, as can be expected, for open-chain diamines the strain energy in the neutral diamine has a negligible effect on basicity enhancement being below 1 kcal·mol^{-1} in all 1,3-propanediamines. The $(HB+SE)^+$ effects (see above) computed using the isodesmic reactions vary from –13.4 to –16.1 kcal·mol^{-1}. The effect is the largest in the unsubstituted 1,3-propanediamine **D9**. The obvious factors are that **D9** is the only base in the row where protonation occurs on primary nitrogen resulting in the strongest HB donor group in the row and the best mutual accessibility of the ammonium and amino groups for HB formation. These two factors outweigh the relative weakness of primary amino group as HB acceptor. The lowest HB stabilising effect is observed in mono- and N,N-disubstituted bases: primary amino group is a weak HB acceptor and neither of the abovementioned factors are operational. It is possible, although somewhat arbitrarily,[49] to separate the $(HB+SE)^+$ contribution into the components by computing the hydrogen bond dissociation energies of model systems presented in Figure 12. The HB energies found are rather coherent with $(HB+SE)^+$ and are in the range of –18.7 to –24.7 kcal·mol^{-1}.

An immediate conclusion from Figure 13 is the extreme compression of the basicity range in AN and THF. In the gas phase the basicity range of the 1,3-propanediamine family is 7.8 pK_a units (ca 10.5 kcal·mol^{-1}) while in THF this range is 2.2 and in AN only 1.1 pK_a units (compression around 3.5 and 7 times, respectively). In very broad terms this is caused by the mutual cancellation of basicity increase due to increased level of substitution and basicity decrease due to decrease of accessibility of the protonated base (in particular, hydrogens attached to the protonated amino centre) for solvent molecules.

Figure 13. Interrelations between the basicities of some of the studied bases in different media.[a]



a — The absolute pK_a values in different media are not directly comparable, so tripropylamine has been used as an arbitrary reference compound for placement of the scales on the figure. The pK_a axis is divided into pK_a units but due to the same reason absolute numbers cannot be added. The insert on bottom left shows expanded view of AN and THF basicities. *b* — pK_α values. *c* — 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 *GB* values (in kcal·mol^{-1}) are given in brackets. Experimental values are used except compounds **B1**, **D6** and **M2**.

In THF the basicity order of 1,3-propanediamines is almost opposite to that in the gas phase (Figure 13). Also, the basicity order of the monoamines is different: N-methylproplyamine is distinctly stronger than propylamine or N,N-dimethylpropylamine. This implies that the preferred centre of protonation in diamines in THF is the methylamino group. Its basicity is enhanced by the one methyl substituent and the one non-hydrogenbonded hydrogen of the protonated form is still available for HB-interaction with a solvent molecule. It is therefore expected that diamines with a methylamino group are protonated on that group. The least attractive protonation centre in THF is the dimethylamino group.

Whether a protonated diamine forms intramolecular HB in THF depends on which of the two possible stabilizing effects — (1) intramolecular HB with low efficiency of solvation or (2) higher efficiency of solvation in the absence of intramolecular HB — prevails (given the low solvation energy of the neutral). THF is a rather strong HB acceptor (B' = 287, β = 0.55, DN = 20.5)[10,11,78,79] and strongly solvates protonated amino groups.

All 1,3-propanediamines except **D3** are by at least one pK_a unit stronger than the respective monoamines indicating stabilisation of the protonated form by intramolecular HB. The fully methylated diamine **D3** is only by 0.3 pK_a units stronger than N,N-dimethylpropylamine, indicating almost complete mutual cancellation of the effects of intramolecular HB formation and more efficient solvation of the non-HB cation. If the intramolecular HB is formed in the protonated form of this base then there will be no proton left for the solvent to form hydrogen bond with.

In AN the basicity order of the monoamines is the same as in THF. Thus the same protonation site preferences are to be expected. The basicity order of 1,3-propanediamines is, however, different from both THF and the gas phase and the basicity range of the substituted 1,3-propanediamines is around 2 times narrower than in THF. The strongest of them is **D6** while **D3** is the weakest. The H-bond acceptor strength of AN (B' = 160, β = 0.31, DN = 14)[11,10,78,79] is significantly lower than that of THF but at the same time it has a smaller molecule size with negatively charged cyano nitrogen readily accessible for solvation. Thus it is expected that **D8** whose high basicity in THF heavily relies on solvation would be relatively weaker in AN than in THF and the bases that have crowded protonation centres — **D3**, **D5** and **D6** — are relatively stronger in AN compared to THF. It is evident from Figure 13 that this is exactly the case. Comparing the basicities of the 1,3-propanediamines and the related monoamines indicates that all protonated 1,3-propanediamines form intra-molecular hydrogen bond in AN. The same conclusion about **D9** has been reached in ref 38.

Basicity changes in the row of α,ω-bis(dimethylamino)alkanes. In the row of α,ω-bis(dimethylamino)alkanes **D1-D4** the basicity in the gas phase increases monotonously. At the same time the length of intramolecular HB in the

protonated bases decreases: in protonated **D1** there is actually no HB and the HB length 1.64 Å in **D4** is the shortest of all diamines studied in this work.

The calculated basicity difference between the diamine and its parent monoamine is the smallest in **D1**: 8.0 kcal·mol^{-1}. The same difference in **D3** and in **D4** is equal: 13.6 kcal·mol^{-1} (experimental: 12.5 and 13.1 kcal·mol^{-1}, respectively). The steric strain in the neutrals due to the repulsion of free electron pairs is low, as can be expected for open-chain compounds, being only for **D2** over 1 kcal·mol^{-1}. The $(HB+SE)^+$ contribution is –8.7 kcal·mol^{-1} for **D2** and rather similar –15.1 and –16.1 kcal·mol^{-1} for **D3** and **D4**, respectively. Separating $(HB+SE)^+$ into the constituent contributions reveals that the stabilization by HB is around 2 times lower in **D2** than in **D3** or **D4**. Also the strain energy in the protonated **D2** is dramatically lower. Out of the diamines studied in this work the strongest HB in the protonated form is observed in **D4**, in accordance with the generalisations presented in ref 72.

1,2-ethanediamine, 1,3-propanediamine and 1,4-butanediamine are less basic than **D2-D4** by 12.4, 10.5 and 9.2 kcal·mol^{-1}, respectively (experimental data). The smaller is the difference, the more stabilising is intramolecular HB in the cation.

In THF medium the span of basicity of **D2-D4** is only 0.3 pK_a units. All three diamines are of approximately the same base strength as the corresponding monoamines. The differences –0.21, 0.18 and 0.03 pK_a units (for **D2**, **D3** and **D4**, respectively) indicate in all these bases intramolecular HB fails to efficiently compete with THF molecules in stabilizing the protonated bases.

In AN **D2-D4** are stronger bases than the parent monoamines by 0.35, 0.99 and 1.69 pK_a units, respectively, meaning that the efficiency of intramolecular HB in stabilizing the protonated base increases from **D2** to **D4**, paralleling the situation in the gas phase. Comparison of **D2-D4** with their non-methylated parent compounds reveals that **D2** is more basic than 1,2-ethanediamine by 0.22 pK_a units, while **D3** and **D4** are weaker than their parent compounds by 0.43 and 0.19 pK_a units, respectively. The trends in water are roughly the same as in AN and THF.

Basicities of bispidines.

In work III the basicity of three bispidine bases **B1**, **B2** and **Sp** was studied.

The rather high basicity of bispidines can be attributed to the destabilization of the neutral base by repulsion between the lone pairs of the facing nitrogen atoms and to the efficient intramolecular bond formation in the protonated bases. Analysis of their gas-phase basicity using the isodesmic reactions approach reveals, that compared to the other diamine bases the strain energies are indeed rather high in the substituted bispidines being 5.3 kcal·mol^{-1} for **B2** and 7.5 kcal·mol^{-1} for **Sp**. The high strain energy in **Sp** is the consequence of additional rigidity introduced by the two cyclohexane rings. The strain energy in **B1** is only 2.3 kcal·mol^{-1}. This is the consequence of the *exo-endo* geometry

of this molecule that eliminates the repulsion of the two lone electron pairs. However, no intramolecular HB is formed in the neutral **B1**: the N···H distance is 2.368Å. The stabilizing joint contribution $(HB+SE)^+$ is similar in **B1** and **B2** (–10.4 and –10.0 kcal·mol^{-1}, respectively), but is smaller in **Sp**: –5.6 kcal·mol^{-1}.

Similarly to earlier findings on different proton sponges[49] the results in work III indicate that release of the steric strain in the neutral base on protonation is not a dominating basicity-increasing factor in bispidines: steric strain energy in the protonated bispidines is higher than in the neutrals. The factor responsible for the enhanced basicity is the intramolecular hydrogen bond.

In AN medium the bispidines are stronger bases than any other of the diamine bases studied in this work thus roughly paralleling the gas-phase situation. The only significant change is the relative weakening of sparteine in AN. In THF substituted bispidines **B2** and **Sp**, which cannot obtain basicity enhancement from stabilisation by solvation, are relatively weak bases compared to the gas phase and **Sp** is again weaker than **B2**. This basicity order reversal is caused first of all by the large molecule size and polarizability of **Sp** vs **B2**. Polarizability is a powerful basicity-enhancing factor in the gas phase but has low effect in solution.[71]

Basicities of Cyclic Diamines. Results in Table 5 reveal that the gas-phase basicity of unsubstituted cyclic diamines is determined by the possibility of intramolecular HB formation in the protonated base. This in turn is determined by the size of the cycle. As seen above the eight-member cycle of **O1** allows easy formation intramolecular HB in the protonated form with the energy of -18.1 kcal·mol^{-1}, which is well in the range observed for 1,3-propanediamines as is the length of the HB: 1.737 Å. Very similar results are found for **O2**. The efficiency of HB in protonated **Hp** (seven-member cycle) is dramatically lower than in **O1**. The stabilizing energy is only –7.1 kcal·mol^{-1} and the bond angle is very low: 111°. In protonated **P1** there is no HB and the ion prefers chair conformation to boat conformation (the former is by 2.1 kcal·mol^{-1} more stable). The basicity order follows the same pattern: **O2** is among the most basic diamines studied in this work, while unsubstituted piperazine is the weakest. N-methylation of piperazine increases its gas-phase basicity as is to be expected.

In solution the basicity-increasing effect of intramolecular HB in the protonated base is lower due to the penalty of losing solvation efficiency. In addition, the cyclic structure of the unsubstituted bases **P1** and **Hp** (no experimental value is available for **O1**) makes their protonated forms easily accessible for solvation. This leads to their rather high basicity in solvents compared to the gas phase. In THF both bases are stronger than tripropylamine, while in the gas phase both are weaker. The tremendous importance of solvation in THF is further demonstrated by the fact that **P1** being in the gas phase the weakest diamine studied in this work has in THF almost the same strength (pK_α = 14.2) as **Sp** (pK_α = 14.3), which in the gas phase is the strongest base studied

in this work! In AN an intermediate situation holds: **P1** and **Hp** are stronger bases than tripropylamine but are distinctly weaker than bispidines or 1,3-propanediamines. Piperidine **Pi1** is in both solvents stronger base than **P1**. N-methylation of **P1** reduces its basicity in both solvents dramatically. The effect of introducing the second methyl group has stronger influence in both solvents indicating that protonation in **P2** occurs on the non-methylated nitrogen in both solvents, paralleling the situation with 1,3-propanediamines.

5.4 Conclusions

Comprehensive basicity study of α,ω-alkanediamines and related bases has been carried out in AN, THF and GP. As a result basicity values for 16, 14 and 9 diamine bases are now available in these three media. In addition the gas-phase basicities and equilibrium geometries were computed for 19 diamino bases at DFT B3LYP 6–311+G** level. The results indicate that basicity in GP is determined by the molecular size and polarizability, the extent of alkylation and by the energy effect of intramolecular hydrogen bond formation in the protonated base. The basicity trends in AN and THF differ very much from those in GP: (1) The solvents severely compress the basicity range of the bases studied (AN 3.9 times and THF 6.9 times) and (2) while stepwise alkylation of the basicity centre leads to a steady basicity increase in the gas phase, the picture is complex in the solvents. Significant differences are also evident between THF and AN. The high hydrogen bond acceptor strength of THF leads to favouring by this solvent the bases with "naked" protonation centres. In particular, the basicity order of N-methylated 1,3-propanediamines is practically inverse to that in the gas phase. The picture in AN is intermediate between that of GP and THF.

6 SUMMARY

The present work focused on expanding of acidity and basicity scales in different media. Also, demonstrating the sources of changes in order of acidities or basicities with the change media and analysing the reasons of these changes are presented.

In the first part of this work the acidity scale in heptane was expanded. Heptane is a solvent with dielectric constant below 2 (D = 1.92) and very weak solvating power toward polar and especially ionic species. The success of the experiments is critically dependent on the base used for deprotonation of acids as well as on the choice of acids. As the result, the acidity scale in heptane has the span about 10 pK_{ip} units. The correlations between heptane and other media showed that heptane is attenuating CH acids 1.2 times compared to gas phase and is found to be a more differentiating solvent than DMSO for NH acids.

The main goal of second part of the work was to extend the existing gas-phase basicity scale of organic compounds towards stronger bases. The scale having a span from 243.7 to 264.6 kcal·mol^{-1} was build during this investigation from which around 15 kcal·mol^{-1} is an extension of the so far existing continuous gas-phase basicity scale of organic bases. For several investigated compounds, the theoretical gas-phase basicities at DFT B3LYP/6–311+G** level were calculated as well and good correlation was found between experiments and calculations. Number of comparisons was also made between basicities in gas phase and different solvents. It appears that correlation of gas-phase and solution basicities can be improved with consideration of size of molecules (as it is one of important factors for the basicity in gas phase).

In the third part the family of bases — α,ω-diaminoalkanes — was investigated in gas phase, tetrahydrofuran and acetonitrile. The main goal was to compare the capability of diaminoalkanes to form the hydrogen bond and its influence to basicity in different media. As a result basicities were measured for 16, 14 and 9 diamine bases in AN, THF and GP, respectively. In addition the gas-phase basicities and equilibrium geometries were computed for 19 diamino bases and 15 related monoamines at DFT B3LYP 6–311+G** level. The effects of the different factors (intrinsic basicity of the amino groups, formation of intramolecular hydrogen bond and molecular strain, etc.) determining diamine basicities were estimated using the method of isodesmic reactions. The results indicate that basicity in GP is determined by the molecular size and polarizability, the extent of alkylation and by the energy effect of intramolecular hydrogen bond formation in the protonated base. The basicity trends in AN and THF differ very much from those in GP: (1) The solvents severely compress the basicity range of the bases studied and (2) while stepwise alkylation of the basicity centre leads to a steady basicity increase in the gas phase, the picture is complex in the solvents. Significant differences are also evident between THF and AN. The high hydrogen bond acceptor strength of THF leads to favouring

by this solvent the bases with "naked" protonation centres. In particular, the basicity order of N-methylated 1,3-propanediamines is practically inverse to that in the gas phase. The picture in AN is intermediate between that of GP and THF.

7 SUMMARY IN ESTONIAN

Happe-aluse tasakaalud vähepolaarsetes keskkondades

Käesolva töö eesmärgiks oli olemasolevate happelisuste ja aluselisuste skaalade laiendamine erinevates keskkondades. Lisaks toodi välja ning analüüsiti põhjuseid, miks happelisuse ja aluselisuse järjestus muutub üleminekul ühest keskkonnast teise.

Antud töö esimeses osas oli eesmärgiks laiendada olemasolevat happelisuse skaalat heptaanis. Oma olemuselt on heptaan apolaarne (D = 1.92) ja seetõttu lahustuvad polaarsed ning ioonsed ühendid heptaanis väga halvasti. Happelisuste mõõtmise edukuse tagab eelkõige osalevate ainete — nii tiitrimisel kasutatava aluse kui ka uuritavate hapete — õige valik. Töö tulemusena laiendati olemasolevat heptaani happelisuse skaalat ligikaudu 10 pK_{ip} ühikuni. Korrelatsioonid heptaani ja teiste keskkondade vahel näitasid, et CH-hapete jaoks on heptaani skaala võrreldes gaasifaasiga 1,2 korda kokku surutum ja NH-hapete jaoks on heptaan parema diferentseeriva võimega kui dimetüülsulfoksiid.

Töö teise osa peamiseks eesmärgiks oli laiendada olemasolevat aluselisuste skaalat gaasifaasis, tugevate orgaaniliste hapete osas. Töö käigus ehitati kooskõlaline aluselisuste skaala ulatusega 243.7 kuni 264.6 kcal·mol^{-1}, millest umbes 15 kcal·mol^{-1} on olemasoleva gaasifaasi orgaaniliste aluste skaala laiendus. Paljudele uuritud alustele arvutati ka teoreetiline gaasifaasi aluselisus DFT B3LYP/6–311+G** tasemel. Eksperimentaalsed ja arvutatud aluselisused leiti olevat heas kooskõlas. Lisaks tehti mitmeid võrdlusi gaasifaasi ning eri solventide aluselisuste vahel. Selgus, et korrelatsioon gaasifaasi ja solvendi aluselisuste vahel paraneb märgatavalt kui võtta arvesse molekuli suurusest tulenevaid muutusi gaasifaasi aluselisustes.

Antud töö kolmadas osas uuriti α,ω-diaminoalkaanide, kui perekonna, aluselisusi tetrahüdrofuraanis, atseetonitriilis ja gaasifaasis. Peamiseks eesmärgiks oli võrrelda diaminoalkaanide võimet moodustada vesinik-sidet ja selle mõju osakaalu aluselisustele eri keskkondades. Töö tulemusna mõõdeti atseetonitriilis, tetrahüdrofuraanis ja gaasifaasis vastavalt 16, 14 ja 9 diamiini aluselisused. Lisaks arvutati aluselisused ja tasakaalugeomeetriad DFT B3LYP 6–311+G** tasemel 19 diamiini ja 15 sarnase monoamiini jaoks. Isodesmiliste reaktsioonide meetodiga hinnati lisaks erinevate faktorite (aminogruppide endi aluselisus, molekulisisese vesiniksideme moodustumine, molekuli steeriline pingestatus jne) osakaalu diamiinide aluselisuse kujunemisel. Tulemused näitavad, et gaasifaasi aluseslise määravad molekuli suurus, polariseeritavus, lämmastike küljes olevate alküülrühmade arv ja energeetiline efekt mis on seotud sisemolekulaarse vesiniksideme moodustumisega. Aluselisuste järjestus solventides erineb tugevasti olukorrast gaasifaasis: (1) solvendid suruvad aluselisuse skaalat tugevalt kokku ja (2) samm-sammuline alküülrühmade lisamine aluselisuse tsentrile, mis

gaasifaasis tõi kaasa ühtlase aluselisuse suurenemise, on solventides tulemuselt märksa ettearvamatum. Märgatavad erinevused on välja toodavad ka tetrahüdrofuraani ja atseetonitriili vahel. Tugeva vesiniksideme aktseptorina eelistab tetrahüdrofuraan aluseid mille protoneerumistsenter pole varjestatud. Silmatorkav on siin näiteks N-metüleeritud 1,3-propaandiamiinide aluselisuste järjekord, mis on sisuliselt vastupidine võrreldes gaasifaasi aluselisustega. Atseetonitriilis on olukord gaasifaasi ja tetrahüdrofuraaniga võrreldes vahepealne.

REFERENCES

1. Olah, G. A.; Prakash, S. K.; Sommer, J. *Superacids;* Wiley: New York, 1985 and references therein.
2. *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley, 1995.
3. Stang, P. J.; White, M. R. *Aldrichimica Acta*, **1983**, *16*, 15–22.
4. Oediger, H.; Möller, F.; Eiter, K. *Synthesis* **1972**, 591–598.
5. Corma, A. *Chem. Rev*. **1995**, *95*, 559–614 and references therein.
6. Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignat'ev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc*. **1994**, *116*, 3047–3057.
7. Burk, P.; Koppel, I. A.; Koppel, I.; Yagupolskii, L. M.; Taft, R. W. *J. Comp. Chem.* **1996**, *17*, 30–41.
8. Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I. *J. Am. Chem. Soc.* **2002**, *124*, 5594–5600.
9. 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.
10. Abboud, J.-L. M.; Notario, R. *Pure Appl. Chem.* **1999**, *71*, 645–718.
11. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 2003 and references therein.
12. *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*, (Palm, V., Ed.), VINITI: Moscow-Tartu, 1975–1985.
13. Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution.* Published as supplement to Pure and Applied Chemistry, Butterworths: London, 1965.
14. a) Leito, I.; Kutt, A.; Kaljurand, I.; Room, E.-I.; Rodima, T.; Koppel, I. A., Abstracts of Papers, 233rd ACS National Meeting, Chicago, IL, United States, March 25–29, **2007**, *INOR-1036*; b) http://tera.chem.ut.ee/~ivo/HA_UT/ .
15. 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.
16. Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem*. **2002**, *67*, 1873–1881.
17. Kaljurand, I.; Rodima, T.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A.; Mishima, M. *J. Org. Chem*. **2003**, *68*, 9988–9993.
18. Kolomeitsev, A. A.; Koppel, I. A.; Rodima, T.; Barten, J.; Lork, E.; Röschenthaler, G.-V.; Kaljurand, I.; Kütt, A.; Koppel, I. A.; Mäemets, V.; Leito. I. *J. Am. Chem. Soc*. **2005**, *50*, 127, 17656 — 17666.
19. Antipin, I. S.; Gareyev, R. F.; Vedernikov, A. N.; Konovalov, A. I. *J. Phys. Org. Chem.* **1994**, *7*, 181–191 and references therein.
20. Streitwieser, A. Jr.; Ciula, J. C.; Krom, J. A.; Thiele, G. *J. Org. Chem.* **1991**, *56*, 1074–1076.
21. Kaufman, M. J.; Gronert S.; Streitwieser A. *J. Am. Chem. Soc.* **1988**, *110*, 2829–2835 and references therein.
22. Yakupolskii, L. M.; Petrik, V. N.; Kondratenko, N. V.; Sooväli, L.; Kaljurand, I.; Leito, I.; Koppel, I. A. *J. Chem. Soc. Perkin Trans. 2.* **2002**, 1950–1955.

23. Leito, I.; Kaljurand, I.; Koppel, I. A.; Yagupolskii, L. M.; Vlasov, V. M. *J. Org. Chem.* **1998**, *63*, 7868–7874.
24. Kütt, A.; Leito, I.; Kaljurand, I.; Sooväli, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A. *J. Org. Chem.* **2006**, *71*, 2829–2838.
25. Kaljurand, I; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019–1028.
26. Koppel, I. A.; Koppel, J.; Pihl, V.; Leito, I.; Mishima, M.; Vlasov, V. M.; Yagupolskii, L. M.; Taft, R. W *J. Chem. Soc., Perkin Trans 2*. **2000**, 1125–1133.
27. Koppel, I. A.; Koppel, J.; Leito, I.; Koppel, I.; Mishima, M.; Yagupolskii, L. M. *J. Chem. Soc., Perkin Trans. 2*. **2001**, 229–232.
28. Leito, I.; Rodima, T.; Koppel, I. A.; Schwesinger, R.; Vlasov, V. M. *J. Org. Chem.* **1997**, *62*, 8479–8483.
29. Conant, J. B.; Wheland, G. W. *J. Am. Chem. Soc.* **1932**, *54*, 1212.
30. McEwewn, W. K. *J. Am. Chem. Soc.* **1936**, *58*, 1124.
31. Streitwieser, A. Jr.; Juaristi, E.; Nebenzahl, L. L. In *Comprehensive Carbanion Chemistry. Part A. Structure and Reactivity*; Buncel, E.; Durst, T., Eds.; Elsevier: Amsterdam, 1980; p 323.
32. http://webbook.nist.gov/chemistry/
33. Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data*. **1998**, *27*, 3, 413–656.
34. *ACS Symposium Series, Vol. 359: Fourier Transform Mass Spectrometry: Evolution Innovation and Applications. [Developed from a Symposium of the American Chemical Society, Anaheim, Calif., September 7–12, 1986]*. Buchanan, M. V., Ed.; American Chemical Society: Washington, DC, 1987.
35. Marshall, A.G.; Hendrickson C.L. *International Journal of Mass Spectrometry*, **2002**, *215*, 59–75.
36. Koppel, I. A.; Suurmaa, E. R.; Pikver, R. J.; Mölder, U. H. *Ion- molecule reactions of organic compounds in gas phase.*, (in Russian, Tolstikov, G. A., Ed.), Akademia Nauk SSSR: UFA, 1987.
37. Mishima, M.; Mustanir; Fujio, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2009–2018.
38. Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005–5010.
39. Barbosa, J., Barrón, D., Buti, S. *Anal. Chim. Acta* **1999**, *389*, 31–42.
40. Kolthoff, I. M.; Chantooni, M. K. Jr. *J. Phys. Chem.* **1968**, *72*, 2270–2272.
41. Schwesinger, R.; Schlemper, H. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167–1169.
42. Bernasconi, C. M.; Leyes, A. E.; Ragains, M. L.; Shi, Y.; Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8632–8639.
43. Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45–92 and references therein.
44. Cookson, R. F. *Chem. Rev.* **1974**, *74*, 5–28.
45. Blanco, S. E.; Ferretti, F. H. *Chem. Phys. Lett.* **2005**, *403*, 400–404.
46. Garrido, G.; Koort, E.; Ràfols, C.; Bosch, E.; Rodima, T.; Leito, I.; Rosés, M. *J. Org. Chem*. **2006**, *71*, 9062–9067.
47. *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.

48. Burk, P.; Koppel, I. A.; Koppel, I.; Leito, I. Travnikova, O. *Chem. Phys. Lett.* **2000**, *323*, 482–489.
49. S. Howard, *J. Am. Chem. Soc.* **2000**, *122*, 8238–8244.
50. 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.
51. Vlasov, V. M; Terehova, M. I.; Petrov, E. S.; Shatenshtein, A. I. *Zh. Org. Khim*. **1981**, *17*, 2025–2031.
52. Bordwell, F. G. *Acc. Chem. Res*. **1988**, *21*, 456–463.
53. Koppel, I.; Koppel, J.; Maria, P.-C.; Gal, J.-F.; Notario, R.; Vlasov, M. V.; Taft, R. W. *Int. J. Mass Spectrom. Ion Processes* **1998**, *175*, 61–69.
54. Koppel, I.A. Unbublished results.
55. Vlasov, V. M.; Zaharova, O. V.; Yakobson, G. G. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.* **1977**, *9*, 127–136.
56. Vlasov, V. M; Petrov, E. S.; Zaharova, O. V.; Shatenshtein, A. I.; Yakobson, G. G. *Zh. Org. Khim*. **1979**, *15*, 138–146.
57. Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463–469.
58. Raczyńska, E. D.; Maria P.-C.; Gal, J.-F.; Decouzon, M.; *J. Phys. Org. Chem*. **1994**, *7*, 725–733 and references therein.
59. Raczyńska, E. D.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Wozniak, K.; Kurg, R.; Carins, S. N. *Trends in Organic Chemistry* **1998**, *7*, 95–103 and references therein.
60. Sooväli, L.; Rodima, T.; Kaljurand, I.; Kütt, A.; Koppel I. A. and Leito. I. *Org. Biomol. Chem.,* **2006,** *4,* 2100–2105.
61. Kisanga, P. B.; Verkade, J. G.; Schwesinger, R. *J. Org. Chem.* **2000,** *65,* 5431–5432.
62. Schwesinger, R., Willaredt, J., Schlemper, H., Keller, M., Schmitt,D., Fritz, H. *Chem. Ber*. **1994**, *127*, 2435–2454.
63. a) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 2699–2701; b) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1972**, *94*, 4726–4728.
64. Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504–3510.
65. Bouchoux, G.; Choret, N.; Berruyer-Penaud, F. *J. Phys. Chem. A* **2001**, *105*, 3989–3994.
66. Alder, R. W.; Arrowsmith, R. J.; Casson, A.; Sessions, R. B.; Heilbronner, E.; Kovač, B.; Huber, H.; Taagepera, M. *J. Am. Chem. Soc.* **1981**, *103*, 6137–6142.
67. Alder, R. W.; *J. Am. Chem. Soc.* **2005**, *127*, 7924–7931.

68. Staab, H. A.; Saupe, T. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 865–879; *Angew. Chem.* **1988**, *100,* 895–909.
69. Galasso, K. Goto, Y. Miyahara, B. Kovač, L. Klasinc, *Chem. Phys.* **2002**, *277*, 229–240.
70. Alkorta, I; Elguero, J. *Struct. Chem.* **2000**, *11*, 335–340.
71. a) Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247–350; b) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1–83.
72. Alder, R. W. *Chem. Rev.* **1989**, *89*, 1215–1223.
73. Hine, J.; Li, W.-Sh. *J. Org. Chem.* **1975**, *40*, 1795–1800.
74. Bouchoux, G.; Buisson, D.-A.; Bourcier, S.; Sablier, M. *Int. J. Mass Spectrom.* **2003,** *228*, 1035–1054.
75. Lau, Y. K.; Saluja, P. P. S.; Kebarle, P.; Alder, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 7328–7333.
76. Toom, L.; Kütt, A.; Kaljurand, I.; Leito, I.; Ottosson, H.; Grennberg, H.; Gogoll, A. *J. Org. Chem*. **2006**, *71*, 7155–7164.
77. Pawlak, Z.; Zundel, G.; Fritsch, J.; Wawrzynow, A.; Kuna, S.; Tusk, M. *Electrohim. Acta* **1984**, *29*, 391–395.
78. Koppel, I.; Palm, V. *Advan. Linear Free Energy Relat.* (Chapman, N. B.; Shorter, J., Eds.), Plenum: London — New York, 1972.
79. Koppel, I. A.; Paju, A. *J. Org. React.* **1974**, *11*, 121–136.

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PUBLICATIONS

I

II

Experimental Gas-Phase Basicity Scale of Superbasic Phosphazenes

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Instrumentation, experimental setup and conditions of FT-ICR experiments

The FT-ICR spectrometric GB measurements were carried out at Kyushu University. Each equilibrium measurement is a measurement of relative basicity of bases B_1 and B_2 (that is "each arrow" in Table S2) according to the eqs 3–5 of the manuscript. The partial pressures of the neutrals were measured using the Bayard-Alpert gauge and were corrected for the differences in ionization cross-sections (see ref 1 for details). Ratio of the intensities of the $M+H^+$ ions in the mass spectrum was used as the estimate of the ratio of partial pressures of the ions. M+ isotope intensity corrections for $M+H^+$ intensities were made when necessary. The eternal problem with introduction of compounds with low volatility is that the conventional leak-valve system is unsuitable for their introduction due to the long "path" from the inlet system (the so-called "oven") to the ICR cell. To solve this problem we used the so-called direct inlet probe. This is a stainless steel rod with diameter around 1 cm. At its end there is a hole with 2 mm diameter to fix a capillary with the compound under study. The rod can be inserted into the ICR spectrometer in such a way that its tip is located at few centimeters from the cell (depending on the depth of introduction). The rod is ´inserted through a differentially pumped vacuum chamber to prevent degradation of the vacuum in the ICR cell. Even the compounds that have low vapor pressures can be vaporized this way to yield sufficient vapor pressure in the cell. The compounds 2, 4, 8, 11, 15, 16, 17, 19, 20, 25–28, 30 were introduced by means of the direct inlet probe.[1] Constant partial pressures of the compounds were obtained by cooling or heating the probe tip. Temperature was taken up slowly, and the temperature was kept constant after the compound's pressure was at appropriate level. Probe tip cooling was achieved by letting nitrogen gas generated from liquid nitrogen flow through the cooling gas canal of the probe. Direct inlet probe tip temperatures and net system pressure for introducing each of these compounds are given in Table S1. Depending on particular compound

it took several hours to several days to enter the ICR cell. The rest of the bases and also 30 in some experiments were introduced from the conventional sample introduction system (the "oven") that was maintained at 150 °C. The ICR cell temperature was kept 100±3 °C.

Table S1. Conditions for introduction of compounds of low volatility.

No	Base	Probe tip temperature (ºC)	Pressure·10^7 (torr)
2	PhP_2(dma)	50–71	4.5–11
4	2-Cl-$C_6H_4P_2$(dma)	61	5.1–7.1
8	4-Me_2N-$C_6H_4P_1$(pyrr)	58–86	2.3–6.5
11	4-MeO-$C_6H_4P_1$(pyrr)	81–112	6.9–7.7
19	4-Br-$C_6H_4P_1$(pyrr)	98–99	4.0–6.9
25	2-NO_2-5-Cl-$C_6H_3P_1$(pyrr)	130	4.7–5.1
26	4-CF_3-$C_6H_4P_1$(pyrr)	87–97	5.7–8.7
27	2,6-Cl_2-$C_6H_3P_1$(pyrr)	83–86	3.3–5.6
28	2-NO_2-4-Cl-$C_6H_3P_1$(pyrr)	126–131	4.4–5.8
30	$PhP_1(dma)_2Me$	45	5

The equilibrium measurements were carried out at different partial pressures of the neutrals. Good agreement was obtained between the $\Delta\Delta G_b$ values. At given partial pressures of the neutrals the equilibrium measurements were carried out as series of pulse sequences with different reaction times. Each sequence consisted of generating ions (by an electron impact pulse from a few to 10 ms), giving them time to react (reaction time) and detecting the ions (see ref 2 for more details). From the ion intensity ratios at different reaction times (and at constant partial pressures of the neutrals) time plots were constructed. From the time plots it was found that between 1 and 20 s of reaction time was necessary to reach the equilibrium (depending on the reacting bases and their partial pressures). To ensure that the equilibrium has been reached reaction times significantly longer that what was required to reach the plateau on the time plot were used in all cases. All experiments were carried out at cell temperatures 373 K.

Determination of pK_{ip}(THF) and pK_α(THF) and pK_a(AN) values

The pK_{ip}(THF) and pK_α(THF) values of 9, 12 and pK_a(AN) values of 4, $PhP_1(dma)_2$tmg and PhP_1(tmg) were determined as follows. The experimental ΔpK_{ip} determination spectrophotometric method in THF has been described in detail earlier[3] and it was used without modifications. The measurements are

relative, i.e. basicity difference (expressed either as ΔpK_{ip} or ΔpK_{α}) of the two bases B_1 and B_2 is studied:

$$\begin{matrix} & K_d^{HB_1^+A^-} & & K & & 1/K_d^{HB_2^+A^-} & \\ B_2 + HB_1^+A^- & \rightleftarrows & B_2 + HB_1^+ + A^- & \rightleftarrows & HB_2^+ + B_1 + A^- & \rightleftarrows & HB_2^+A^- + B_1 \end{matrix} \quad (1)$$

The K_d–s are the dissociation constants of the respective ion pairs. The directly measured quantity is the relative ion-pair basicity – ΔpK_{ip} – of bases B_1 and B_2. It is expressed as follows:

$$\Delta pK_{ip} = pK_{ip}(HB_2^+A^-) - pK_{ip}(HB_1^+A^-) = \log\frac{K \cdot K_d^{HB_1^+A^-}}{K_d^{HB_2^+A^-}} = \log\frac{a(HB_2^+A^-)\cdot a(B_1)}{a(HB_1^+A^-)\cdot a(B_2)} \quad (2)$$

The K_d values were estimated using the Fuoss equation as described in refs 3 and 17. Ionic radii are given in Table S5 in Supporting Information. Using the K_d values the pK_{α} (an estimate of the pK_a) can be found as follows:

$$\Delta pK_{\alpha} = pK_{\alpha}(HB_2^+) - pK_{\alpha}(HB_1^+) = \Delta pK_{ip} - \log\frac{K_d^{HB_1^+A^-}}{K_d^{HB_2^+A^-}} \quad (3)$$

The pK_a determination method in AN is in principle similar to that in THF. The only difference is that the ΔpK_a is obtained directly from experimental data (for details see refs 6, 3, **7**).

$$B_2 + HB_1^+ \quad \rightleftarrows \quad HB_2^+ + B_1 \quad (4)$$

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

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

The preparation of solutions in THF and AN, and titration experiments were carried out in a professional glovebox in argon atmosphere, where the contents of O_2 and H_2O were less than 1 ppm. Solutions of methanesulfonic acid (in THF) and triflic acid (in AN) were used as acidic and solution of $EtP_2(dma)$ (in both solvents) was used as basic titrant. The measurements were carried out in an external cell compartment, situated in the glovebox. The cell compartment was connected to the UV-Vis spectrophotometer by means of two quartz fiber

optic cables. For both solvents the new experimental results are given in Table 2 in the main text.

Table S2. Experimental and Calculated Gas-Phase Basicities, and Experimental Basicities in THF, AN and water.

No	Base	Directly measured $\Delta\Delta G_b$ [a]	GB_{exp} [b]	GB_{calc} [c]	pK_{ip}(THF) [c]	pK_a(THF) [c]	pK_a(AN) [g]	$pK_a(H_2O)$ [n]
1	EtP_2(dma)		1106.9	1112.5	24.9	25.3	32.94 [m]	
2	PhP_2(dma)		1094.9	1084.5 [f]	19.4	19.8	26.46	
3	Verkade-iBu_3		1091.2				33.58 [i]	
4	2-Cl-$C_6H_4P_2$(dma)		1089.8	1082.4	15.8 [f]	16.3 [f]	24.23 [h]	
5	EtP_1(pyrr)		1085.9	1078.6	21.7	21.7	28.88	
6	Verkade-Me_3		1083.8	1066.9			32.90 [i]	
7	t-BuP_1(pyrr)		1082.5	1080.3	20.2	20.2	28.42	
8	4-Me_2N-$C_6H_4P_1$(pyrr)		1077.3		17.3	17.3	23.88	12.00
9	BEMP		1071.2	1069.4	19.3 [h]	19.0 [h]	27.63 [l]	
10	HP_1(pyrr)		1067.7	1066.9 [f]	20.8	20.8	27.01	
11	4-MeO-$C_6H_4P_1$(pyrr)		1066.6		16.8	16.8	23.12	11.94
12	t-$OctP_1$(dma)		1063.7		18.5	18.5	26.49 [l]	
13	t-BuP_1(dma)		1058.0	1054.8	18.9 [h]	18.9 [h]	26.98	
14	MeP_1(dma)		1054.0	1055.6 [k]	20.7	20.7	27.52	
15	PhP_1(pyrr)		1053.0	1049.8	16.1	16.1	22.34	11.52
16	1-NaphthP_1(pyrr)		1050.1		14.2 [d]	14.2 [d]	20.61	
17	2-Cl-$C_6H_4P_1$(pyrr)		1049.2		13.2 [d]	13.2 [d]	20.17	9.98
18	HP_1(dma)		1044.6	1044.3 [k]	19.7	19.7	25.85	
19	4-Br-$C_6H_4P_1$(pyrr)		1043.1		15.4 [d]	15.4 [d]	21.19	11.23
20	2,5-Cl_2-$C_6H_3P_1$(pyrr)		1038.8	1021.7	11.9 [d]	11.9 [d]	18.52	9.21
21	ITBD		1037.2	1042.2				
22	ETBD		1035.7	1026.3				
23	MTBD [j]		1030.2 [l]	1037.6	18.6	18.6	25.44 [l]	
24	PhP_1(dma)		1029.9	1026.3 [f]	15.2 [d]	15.2 [d]	21.25	10.64
25	2-NO_2-5-Cl-$C_6H_3P_1$(pyrr)		1028.5		10.1 [d]	10.1 [d]	17.27	8.33
26	4-CF_3-$C_6H_4P_1$(pyrr)		1026.8		14.6 [d]	14.6 [d]	20.16	10.65
27	2,6-Cl_2-$C_6H_3P_1$(pyrr)		1026.3	1035.5	11.8 [d]	11.8 [d]	18.56	9.00
28	2-NO_2-4-Cl-$C_6H_3P_1$(pyrr)		1024.9	1030.9	10.8 [d]	10.8 [d]	17.68	8.37
29	2-Cl-$C_6H_4P_1$(dma)		1019.9	1017.5	12.5 [d]	12.5 [d]	19.07	
30	PhP_1(dma)$_2$Me		1019.7	1015.5	15.4	15.4	21.03	

[a] Directly measured experimental $\Delta\Delta G_b$ (kJ/mol) values obtained from FT-ICR measurements. [b] Estimated 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] Reference 3. [e] Reference 4. [f] Reference 5. [g] Reference 6 if not noted otherwise. [h] Present work. [i] Reference 8. [j] anchor of the scale, GB value taken from ref 9. [k] Reference 10. [l] Reference 11. [m] Reference 12. [n] Reference 13

Table S3. Results of Calculations of Gas-Phase Basicity (GB) in kJ/mol of Some Strong Bases at DFT B3LYP/6-311+G** Level and experimental basicity values in various media.[a]

No		Neutral			Protonated Form									
		E	H	G	E	H	G	GB_{calc}	PA(B)	GB_{exp}	pK_a(AN)[c]	pK_{ip}(THF)[e]	pK_a(THF)[e]	$pK_a(H_2O)$[l]
18	HP_1(dma)	−800.5860	−800.3049	−800.3633	−801.0065	−800.7110	−800.7704	1044.3[d]	1072.4[d]	1044.6	25.85	19.7	19.7	
14	MeP_1(dma)							1055.6[d]		1054.0	27.52	20.7	20.7	
13	t-BuP_1(dma)	−957.8684	−957.4703	−957.5408	−958.2952	−957.8820	−957.9527	1054.8	1087.0	1058.0	26.98	18.9	18.9	
9	BEMP	−1074.6385	−1074.1731	−1074.2486	−1075.0709	−1074.5904	−1074.6661	1069.4	1102.1	1071.2	27.63	19.3	19.0	
10	HP_1(pyrr)	−1032.9040	−1032.5106	−1032.5781	−1033.3353	−1032.9270	−1032.9947	1066.9[d]	1099.6[d]	1067.7	27.01	20.8	20.8	
5	EtP_1(pyrr)	−1111.5381	−1111.0853	−1111.1616	−1111.9763	−1111.5083	−1111.5826	1078.6	1116.7	1085.9	28.88	21.7	21.7	
7	t-BuP_1(pyrr)	−1190.1862	−1189.6758	−1189.7543	−1190.6244	−1190.0986	−1190.1760	1080.3	1048.5	1082.5	28.42	20.2	20.2	
30	$PhP_1(dma)_2Me$	−937.0049	−936.6867	−936.7518	−937.4162	−937.0837	−937.1488	1015.5	1048.5	1019.7	21.03	15.4	15.4	
24	PhP_1(dma)	−1031.6909	−1031.3243	−1031.3947	−1032.1055	−1031.7246	−1031.7958	1026.3[d]	1069.4[d]	1029.9	21.25	15.2	15.2	10.64
29	2-Cl-$C_6H_4P_1$(dma)	−1491.3147	−1490.9563	−1491.0309	−1491.7268	−1491.3542	−1491.4286	1017.5	1051.0	1019.9	19.07	12.5	12.5	
15	PhP_1(pyrr)	−1264.0093	−1263.5301	−1263.6094	−1264.4344	−1263.9406	−1264.0195	1049.8	1057.3	1053.0	22.34	16.0	16.0	11.52
27	2,6-Cl_2-$C_6H_3P_1$(pyrr)	−2183.2545	−2182.7916	−2182.8755	−2183.6406	−2183.1924	−2183.2800	1035.5	1060.2	1026.3	18.56	11.8	11.8	9.00
20	2,5-Cl_2-$C_6H_3P_1$(pyrr)	−2183.2599	−2182.7996	−2182.8878	−2183.6746	−2183.1998	2183.2872	1021.7		1038.8	18.52	11.9	11.9	9.21
28	2-NO_2–4-Cl-$C_6H_3P_1$(pyrr)	−1928.1929	−1927.7170	−1927.8058	−1928.6109	−1928.1206	−1928.2084	1030.9	1066.1	1024.9	17.68	10.8	10.8	8.37
	PhP_1(tmg)	−1714.1506	−1713.4838	−1713.6005	−1714.6137	−1713.9313	−1714.0474	1146.4	1181.1		31.4	23.7	24.3	
1	EtP_2(dma)	−1544.6159	−1544.0909	−1544.1839	−1545.0661	−1545.5251	−1545.6178	1112.5	1146.4	1106.9	32.94	24.9	25.3	
2	PhP_2(dma)	−1697.0862	−1696.5346	−1696.6319	−1697.5243	−1696.9575	−1697.0551	1084.5[d]	1116.7[d]	1094.9	26.46	19.4	19.8	
4	2-Cl-$C_6H_4P_2$(dma)	−2156.7092	−2156.1658	−2156.2658	−2157.1462	−2156.5876	−2156.6882	1082.4	1113.8	1089.8	24.23	15.8	16.3	
6	N, N', N" – Me_3Verkade's Base	−916.0987	−915.7722	−915.8297	−916.5316	−916.1899	−916.2463	1066.9	1102.9	1083.8	32.90[i]			
3	N, N', N" – i-Bu_3Verkade's Base									1091.2	33.58[i]			
	TBD	−438.9452	−438.7307	−438.7736	−439.3616	−439.1322	−439.1767	1031.4	1060.2	1022.1[b]	26.03	21.7	21.0	
23	MTBD	−478.2595	−478.0161	−478.0626	−478.6782	−478.4195	−478.4680	1037.6	1065.2	1030.2[b]	25.49	18.6	18.0	
22	ETBD	−517.5850	−517.3119	−517.3617	−518.0053	−517.7169	−517.7676	1026.3	1069.4	1035.7				
21	ITBD	−556.9052	−556.6031	−556.6559	−557.3264	−557.0089	−557.0631	1042.2	1071.5	1037.2				
	DBD	−422.8978	−422.6722	−422.7152	−423.3116	−423.0709	−423.1144	1020.9	1053.1	1014.0[b]				
	DBU	−462.2167	−461.9611	−462.0072	−462.6267	−462.3558	−462.4020	1009.6	1042.2	1015.5[b]	24.34	18.1	16.9	
	DBN	−383.5734	−383.9778	−383.4188	−383.9841	−383.7736	−383.4148	1012.5	1045.6	1005.9[b]	23.79			
	TTT	−570.5172	−570.2722	−570.3199	−570.9511	−570.6911	−570.7399	1076.1	1106.2	1066.3[f]	26.22[h]			
	Guanidine							964.8[d]	993.7[d]	949.4[b]				
	TMG							1007.1[d]	1038.5[d]	997.4[b]	23.3	17.0	15.5	
	PhTMG	−593.8014	−593.5187	−593.5763	−594.2098	−593.9122	−593.9697	1006.3	1039.3	1006.0[b]	20.84	15.0	14.0	
	NH_3							817.6[m]		819.0[b]	16.46[k]			
	$MeNH_2$							864.8[m]		864.5[b]	18.37[k]			
	H_2NNH_2	−111.9106	−111.8531	−111.8792	−112.2505	−112.1783	−112.2056	830.1	859.8	822.4[b]	16.48[k]			

No		Neutral			Protonated Form								
		E	H	G	E	H	G	GB_{calc}	PA(B)	GB_{exp}	pK_a(AN)[c]	pK_{ip}(THF)[e]	pK_a(THF)[e]	pK_a(H_2O)[l]
	$NCNH_2$	–148.8349	–148.7964	–148.8246	–149.1533	–149.1037	–149.1327	782.0	813.0	774.9[b]	4.0[k]			
	$(CF_3)_3CNH_2$	–1107.3140	–1107.2222	–1107.2754	–1107.6194	–1107.5132	–1107.5669	738.1	770.3	752.9[b]				
	$CF_3CH_2NH_2$	–433.0506	–432.9737	–432.0105	–433.3804	–433.2889	–433.3259	801.2	833.5	812.9[b]	11.81[k]			
	$PhCH_2NH_2$	–327.0026	–326.8490	–326.8889	–327.3682	–327.1997	–327.2398	894.5	927.2	879.4[b]	16.91			
	4-MeO-Aniline	–402.2407	–402.0825	–402.1249	–402.5957	–402.4226	–402.4662	872.4	899.1	868.5[b]	11.86	8.3	6.5	
	2-Me-Aniline	–327.0142	–326.8618	–326.9033	–327.3656	–327.1984	–327.2416	866.5	889.9	859.1[b]	10.50	6.9	5.1	
	Aniline							855.2[m]		850.6[b]	10.62	7.0	5.2	
	4-CF_3-Aniline	–624.8398	–624.7084	–624.7548	–625.1714	–625.0252	–625.0743	812.1			8.03			
	4-NO_2-Aniline									834.2[b]	6.22			
	1-Napht-NH_2									875.1[b]	9.77			
	Pyrrolidine	–212.6460	–212.5110	–212.5465	–213.0217	–212.8714	–212.9052	915.0	952.7	915.3[b]	19.56	15.3	13.5	
	Me_3N							911.7[m]		918.1[b]	17.61[k]			
	Et_3N	–292.4972	–292.2822	–292.3268	–292.8866	–292.6556	–292.7004	954.0	987.0	951.0[b]	18.82	14.0	12.5	
	$NCNMe_2$	–227.4680	–227.3704	–227.4065	–227.8084	–227.6989	–227.7357	837.6	868.6	821.4[b]				
	Ph_3N	–749.8854	–749.5924	–749.6518	–750.2444	–749.9371	–749.9958	875.7		876.4[b]				
	N,N-Me_2-Aniline (DMA)	–366.3141	–366.1318	–366.1749	–366.6837	–366.4866	–366.5296	904.6	937.6	909.2[b]	11.43	6.5	4.9	
	4-MeO-DMA									922.4[b]				
	4-H_2N-DMA	–421.6861	–421.4860	–421.5321	–422.0683	–421.8543	–421.8998	938.5 (Me_2N)	972.8 (Me_2N)	928.4[b]				
	Proton Sponge	–653.9755	–653.6677	–653.7327	–654.3793	–654.0577	–654.1149	1000.4	1030.1	995.8[b]	18.62	11.6	11.1	
	4-Me_2N-Pyridine	–382.3601	–382.1894	382.2326	282.7573	382.5721	382.6152	977.8	1010.9	971.1[b]	17.95	13.0	11.2	
	4-NH_2-Pyridine	–303.6564	–303.6207	–303.7324	–304.1214	–303.9953	–304.0304	955.2	989.5	947.8[b]	17.62			
	3-NH_2-Pyridine	–303.7275	–303.6160	–303.6518	–304.1057	–303.9800	–304.0164	930.5	961.9	922.6[b]	14.17			
	2-NH_2-Pyridine	–303.7383	–303.6266	–303.6623	–304.1132	–303.9877	–304.0238	934.3	951.4	915.3[b]	14.47			
	2,6-Me_2-Pyridine	–327.0134	–326.8619	–326.9038	–327.3943	–327.2285	–327.2719	939.7	968.6	931.1[b]	14.13	8.8	7.2	
	4-MeO-Pyridine	–362.9109	–362.7823	–362.8210	–363.2913	–363.1485	–363.1875	935.5	967.8	929.8[b]	14.23	9.1	7.3	
	2-MeO-Pyridine	–362.9209	–362.7923	–362.8313	–363.2904	–363.1477	–363.1868	906.3	939.3	902.8[b]	9.93			
	2-Me-Pyridine	–287.6824	–287.5598	–287.5969	–288.0570	–287.9210	–287.9563	917.1	954.8	917.3[b]	10.50	8.1	6.3	
	Pyridine	–248.3512	–248.2576	–248.2902	–248.7191	–248.6112	–248.6433	900.4	934.3	898.1[b]	12.53	7.3	5.5	
	3-Cl-Pyridine	–707.9726	–707.8874	–707.9235	–708.3308	–708.2316	–708.2678	877.0	910.0	871.5[b]	9.55			
	2-Cl-Pyridine	–707.9766	–707.8914	–707.9274	–708.3323	–708.2332	–708.2694	871.1	903.7	869.0[b]	6.79			
	Imidazole							912.1[m]		909.2[b]	14.99[k]			
	Me_3P							917.6[d]	949.3[d]	926.3[b]			8.7[j]	
	Et_3P	–579.1295	–578.9198	–578.9677	–579.5108	–579.2896	–579.3381	945.6	977.0	952.0[b]			8.5[j]	
	$MePh_2P$	–844.7201	–844.4872	–844.5433	–845.0988	–844.8545	–844.9097	935.1	970.7	939.7[b]	9.96		6.4[j]	
	Ph_3P	–1036.4961	–1036.2077	–1036.2670	–1036.8790	–1036.5794	–1036.6399	852.3	982.0	940.4[b]	7.61			
	Me_2PhP	–652.9421	–652.7658	–652.8115	–653.3175	963.1298	–653.1764	931.4	961.9	936.8[b]			6.0[j]	

[a] Value from this work or from ref 4 if not noted otherwise. [b] Reference 9. [c] References 6, 11, 12 if not noted otherwise. [d] References 5 and 10. [e] Reference 3, 4, 5. [f] Reference 14. [g] Reference 15. [h] Reference 16. [i] Reference 8. [j] Reference 17. [k] Reference 18, 19. [l] Reference 13. [m] Reference 20

Correlations of GB_{exp} with solution basicities. It is of great interest to observe the influence of different media on the acid-base properties of bases in general view and also what is different when one takes a look on some particular family (e.g. phosphazenes). The solvent influence on compounds basicity can be observed by correlating the basicity values in the gas-phase and solvent. The correlation equation has the following form:

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

where pK(X) denotes basicity value in a solvent X, a and b are the slope and intercept, respectively. The correlation results for various sets of compounds from this work and Table S3 are presented in Table S4.

Table S4. The Correlation of Gas-Phase Basicities (GB) with respective solution basicity values (pK(X)) in Solution According to Eq 1.

pK(X)		a	$s(a)$	b	$s(b)$	S	R^2	n	a/5.705[a]
pK_{ip}(THF)	All bases	11.57	1.38	839.3	21.4	41.7	0.639	42	2.03
	All non-phosphazenes	10.42	1.63	818.8	21.2	31.5	0.732	17	1.83
pK_{α}(THF)	All bases	10.63	0.92	860.1	13.4	34.8	0.748	47	1.86
	All phosphazenes	5.17	0.85	968.7	14.6	16.0	0.615	25	0.91
	P_1(pyrr) series	5.137	0.741	972.5	11.7	10.0	0.800	14	0.90
	4-X-PhP_1(pyrr) series	18.28	0.63	760.2	10.1	1.4	0.997	5	3.20
	All non-phosphazenes	8.46	1.37	861.4	14.9	31.0	0.657	22	1.48
pK_a (AN)	All bases	10.94	0.79	768.6	16.0	45.1	0.742	68	1.92
	All phosphazenes	5.021	0.712	937.0	17.0	14.5	0.684	25	0.88
	P_1(pyrr) series	5.163	0.617	938.0	13.8	8.6	0.854	14	0.91
	4-X-PhP_1(pyrr) series	13.21	0.77	761.0	17.0	2.3	0.990	5	2.31
	All non-phosphazenes	9.505	0.971	774.9	17.1	43.2	0.700	43	1.67
	Pyridines	9.118	1.146	796.7	14.7	14.5	0.864	12	1.60
	PhTMG series	13.08	3.43	737.7	70.7	3.7	0.879	4	2.29

[a] The attenuation factor calculated from the slope is a/ 2.30RT = a/5.705.

Correlation GB_{exp} with pK_{ip}(THF) and pK_{α}(THF). The overall correlation between GB and pK_{α}(THF) is rather poor. This can be explained by the large variation in the molecular structure and size of the molecules of compounds correlated. The same conclusion is true for the correlation of all phosphazene bases in which the correlation coefficient is even poorer. From this correlation of GB with pK_{α}(THF) it appears that in global view, for the current data set the gas phase is equal or up to 2 times better differentiating medium of basicities compared to THF. On the other hand, for 4-substituted PhP_1(pyrr) series, where access of the solvent molecule into the protonation center is not affected by the substituents in the phenyl ring the same correlation is excellent and for this series the gas phase is 3.20 times better differentiating medium of basicities than THF. It can be concluded that for

the PhP_1(pyrr) series moderate variation of the molecule size (or volume) H vs MeO or Me_2N in the periphery relative to the protonation center does not have substantial influence on the size, as it can be understood in terms of size-enhanced cation stabilization ability in the gas-phase. According to the 4-X-PhP_1(pyrr) series correlation equation the HP_1(pyrr), EtP_1(pyrr) and t-BuP_1(pyrr) are in THF 4.0, 4.1 and 2.7 pK_α units stronger bases than expected. Thus, substitution of H (or Et) with t-Bu or Ph lowers the cation solvation stabilization by solvent by 1.3 and 4 pK_α units, respectively. Next, when going from PhP_1(pyrr) to 1-$NaphtP_1$(pyrr) or introducing one or several Cl substituents into the *ortho* position of the phenyl ring the additional loss of stabilization is 1.7 and from 2.6 to 3.3 pK_α units, respectively. The largest loss of stabilization is due the introduction of NO_2 into the *ortho* position of the phenyl ring: 3.7 to 4.6 pK_α units. It can be concluded, that the stabilization of protonated molecule by solvation is strongly influenced by immediate vicinity of the protonation center, more precisely its steric hindrance ability.

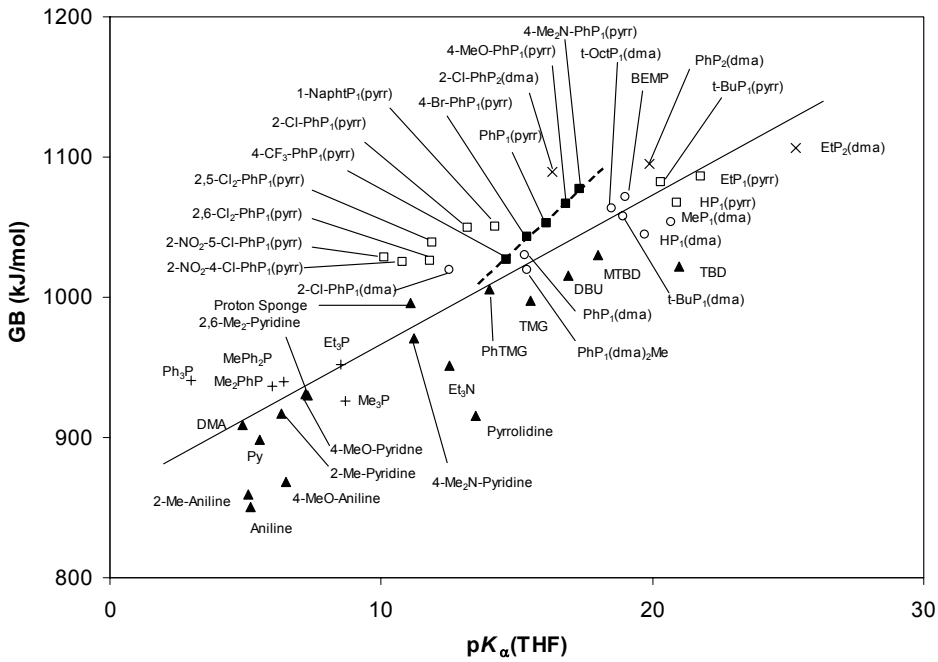


Figure S1. Comparison of the basicity values in THF (pK_α values) and in the gas phase (GB). The solid line corresponds to overall correlation (all available data included), P_1(pyrr) phosphazenes (14 compounds) from present work are denoted by □, from which 4-X-PhP_1(pyrr) phosphazenes by ■, P_2(dma) phosphazenes by ×, P_1(dma) phosphazenes by ○, N bases ▲, and phosphines by +, respectively. The dashed line corresponds to the sub-series of 4-X-PhP_1(pyrr) phosphazenes.

Review of the most deviating points reveals that for many small molecules the correlation strongly overestimates the GB value. Examples are (in brackets: deviation of the experimental GB from the overall correlation line in kJ/mol): pyrrolidine (–88.4), aniline (–64.8) and 4-methoxyaniline (–60.8). The large molecules on the other hand tend to have their GB values underestimated by the correlation. 2-NO_2-5-Cl-$C_6H_3P_1$(pyrr) (61.0), 2-Cl-$C_6H_4P_2$(dma) (56.3) and 2-NO_2-4-Cl-$C_6H_3P_1$(pyrr) (49.9) serve as examples. This leads to the idea of including the molecule/ion size in the correlation according to the following equation:

$$\mathrm{GB(kJ/mol)} = a_1\, \mathrm{p}K(\mathrm{X}) + a_2\, r + b \qquad (7)$$

where r is the mean ionic radius of the protonated base. Radii used in this correlation for these compounds are given in Table S5.

Table S5. Ionic Radii of the Protonated Forms of the Bases and Methanesulfonate Anion.

ion	ion-pair radius, Å[a]	Ion	ion-pair radius, Å[a]
R'P_1(pyrr)H^+, R'P_1(dma)H^+; R'P_1(dma)$_2$MeH^+, BEMPH^+	4	TBDH^+, MTBDH^+, ETBDH^+, ITBDH^+, PhosphinesH^+	3
R'P_2(dma)H^+	4.8	PhP_1(dma)$_2$tmg	4.5
DBUH^+	2.5	PhTMGH^+	2.7
TMGH^+; Et_3NH^+, N,N-Me_2-AnilineH^+, 2,6-X_2-PyridineH^+	2.2	X-AnilineH^+; X-PyridineH^+, PyrrolidineH^+	2
DMANH^+	3.2	$CH_3SO_3^-$	2.5

[a] Ionic radii from previous works (ref 3, 5, 17) or this work. In cases when no data were available, the radii were estimated by PM3 calculations; R' = alkyl, aryl or H; X = substituent in phenyl ring.

This correlation leads to the following results: GB(kJ/mol) = 6.06 pK_α(THF) + 41.7 r + 783.0, the standard deviations of the term a_1, a_2 and b are 0.72, 4.46 and 11.5, respectively, indicating the significance of all the parameters in the correlation (see Table S6). Inclusion of the size parameter r into the correlation equation of pK_α(THF) and GB_{exp} improves the overall correlation in terms of S and R^2, from 34.8 to 20.6 and from 0.748 to 0.914 respectively. The radius r effectively takes into account the molecular volume/polarizability. It has been demonstrated[21] that molecular polarizability is an important parameter in determining reactivity in the gas phase and that it has lower influence on reactivity in condensed phase.

Table S6. Correlation Results for All Compounds According to Eq 2 Including Size Parameter *r*.

p*K*(X)	a_1	$s(a_1)$	a_2	$s(a_2)$	b	$s(b)$	S	R^2	n
pK_α(THF) all compounds	6.06	0.72	41.7	4.46	783.0	11.5	20.6	0.914	47
pK_α(THF) all phosphazenes	4.21	0.77	37.2	11.0	832.4	42.1	13.3	0.746	25
pK_α(THF) all non-phosphazenes	7.29	1.16	41.8	12.2	770.5	29.7	25.7	0.777	22
pK_a(AN) all compounds	5.890	0.545	41.27	3.98	747.9	9.4	20.2	0.932	59
pK_a(AN) all phosphazenes	4.152	0.643	34.19	10.07	817.4	37.9	12.0	0.792	25
pK_a(AN) all non-phosphazenes	6.432	0.822	40.71	10.03	740.5	18.3	23.9	0.888	34

Similar trends, although not as extensive are observed also for the separate correlation sets of phosphazene and non-phosphazene bases (see Tables S4 and S6). Inclusion of the reciprocal (r^{-1}) or reciprocal of square (r^{-2}) of the size parameter r into the correlation equation 7 instead of r will not lead to improvement of the statistical parameters of the correlations.

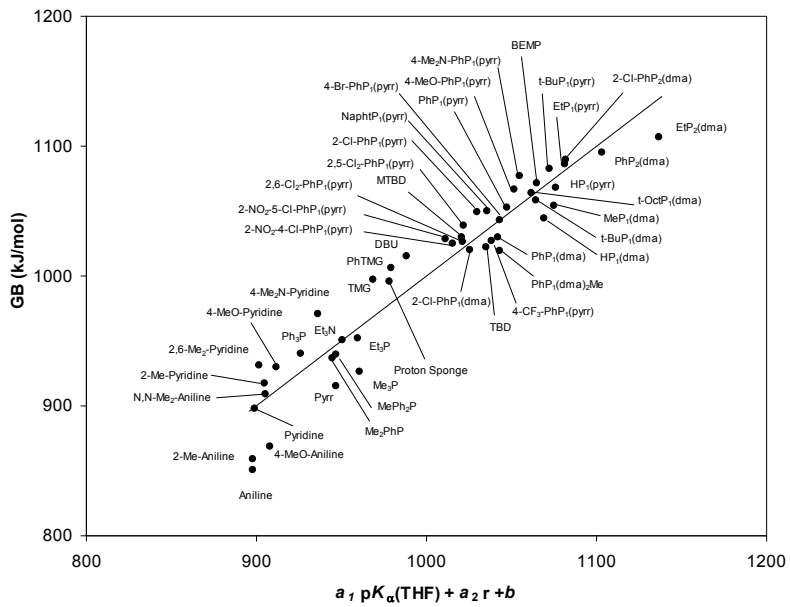


Figure S2. Correlation of the term a_1 pK_α(THF) + a_2 r +b and the Gas-phase Basicity (GB). The solid line corresponds to overall correlation.

Correlation of GB_{exp} with pK_a(AN) and pK_a(H_2O). The overall pattern of correlation of the GB values with pK_a values in AN is similar to THF (see Figure S3).

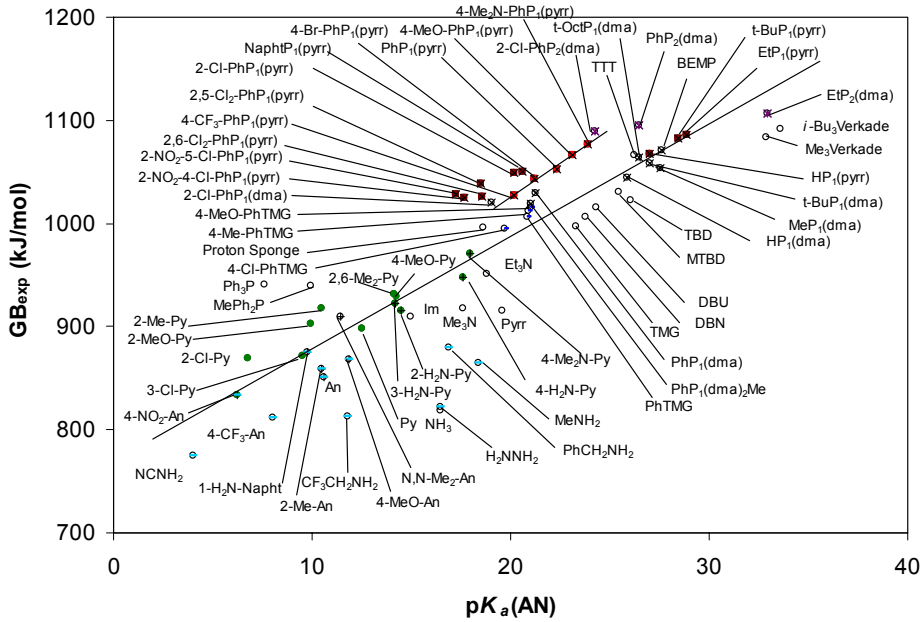


Figure S3. Correlation of the basicity values in AN (pK_a values) and in the Gas Phase (GB). The solid line corresponds to overall correlation (all available data).

Molecular size plays an important role in this correlation as well. Correlation according to the eq 6 leads to the following results: GB_{exp} = 10.94 pK_a(AN) + 768.6, the standard deviations of the slope and intercept are 0.79 and 16.0, respectively, R^2 = 0.742; n = 68 and S = 45.1. Inclusion of molecule size parameter according to eq 7 gives GB_{exp} = 5.89 pK_a(AN) + 41.3 r + 747.9, the standard deviations of the terms a_1, a_2 and b are 0.55, 3.98 and 9.4, respectively, R^2 = 0.932; n = 59 and S = 20.2. See Figure S4. Thus, including the molecule size in the correlation leads to a significant improvement in this solvent also. For the 4-substituted PhP_1(pyrr) series eq 6 is GB_{exp} = 13.21 pK_a(AN) + 761.0, the standard deviations of the slope and intercept are 0.77 and 17.0, respectively, R^2 = 0.990; n = 5 and S = 2.3. Term a/5.705 equals 2.31, that is gas phase is 2.31 times better differentiator of basicities of 4-X-PhP_1(pyrr) series than AN.

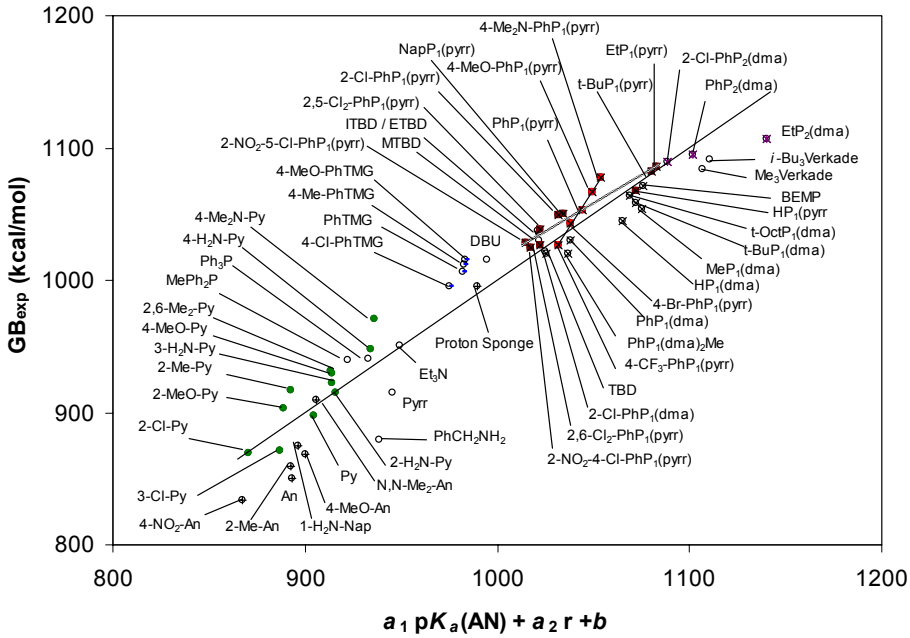


Figure S4. Correlation of the term a_1 pK_a(AN) + a_2 r +b and the Gas-phase Basicity (GB). The solid line corresponds to overall correlation (all available data).

Recently the pK_a values for a set of P_1 arylphosphazenes in water have been published.[13] Their pK_a values were found to be between 6 and 12 in water, meaning that in relative terms they are significantly weaker bases in water than in the gas phase. As an example: phenyltetramethylguanidine (GB_{exp} = 1006.0 kJ/mol, pK_a(H_2O) = 11.77) is a significantly weaker base in the gas phase than any of the studied P_1 arylphosphazenes and at the same time beats most of them in the aqueous medium. Correlating the gas-phase data of this work with the pK_a(H_2O) from ref 13 gives: GB(kJ/mol) = 10.32 pK_a(H_2O) + 938.0, the standard deviations of the slope and intercept are 2.58 and 26.6, respectively, R^2 = 0.667; n = 10 and S = 11.1. For the 4-X-PhP$_1$(pyrr) series the equation is as follows: GB(kJ/mol) = 34.96 pK_a(H_2O) + 652.5, the standard deviations of the slope and intercept are 3.72 and 42.7, respectively, R^2 = 0.967; n = 5 and S = 4.1. Term a/5.705 equals 6.1, meaning that the gas phase is 6.1 times better differentiator of basicities of the 4-X-PhP$_1$(pyrr) series than water. Although the correlation parameters of 4-X-PhP$_1$(pyrr) series for water are not as good as for THF and AN the certain trend of the influence *ortho* substituent hindrance can be observed also in comparison of this medium with the gas phase, see Figure S5.

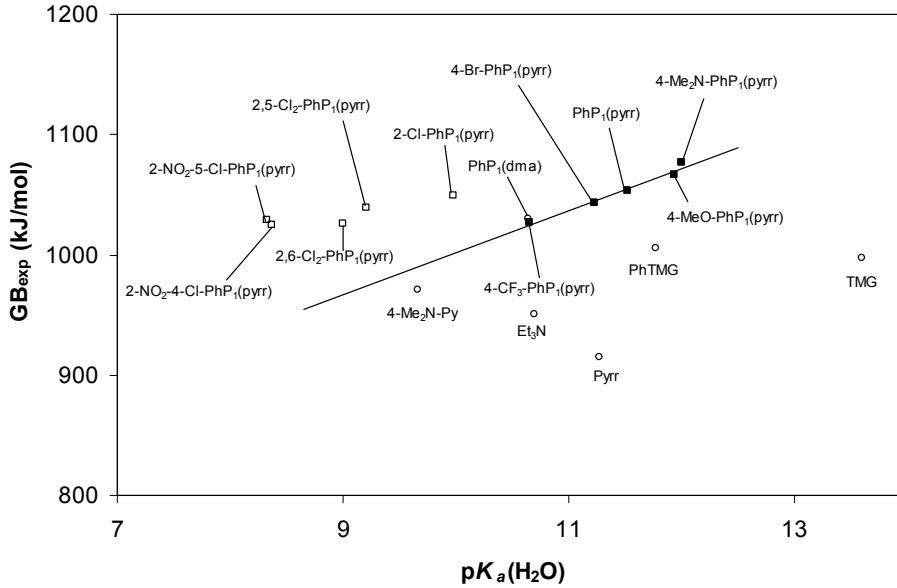


Figure S5. Correlation of the basicity values in water (pK_a values) and in the Gas Phase of P_1(pyrr) series and some other bases. The solid squares and solid line corresponds to P_1(pyrr) compounds, open circles for some reference compounds. pK_a(H_2O) data from ref 13**.**

Influence of the structure variation on the solvation of P_1(pyrr) series. Previously we have studied[6] influence of the structure variation on the pK values of the P_1(pyrr) phosphazene series in AN and THF. The overall correlation from the literature data[6] given in Table S7 is: pK_α(THF) = 0.96 pK_a(AN) – 5.8, the standard deviations of the slope and intercept are 0.04 and 0.8, respectively, R^2 = 0.976; n = 19 and S = 0.67. For 4-X-PhP_1(pyrr) series the equation is as follows: pK_α(THF) = 0.74 pK_a(AN) – 0.4, the standard deviations of the slope and intercept are 0.02 and 0.5, respectively, R^2 = 0.996; n = 6 and S = 0.10. This correlation supports the above-made observation, that when comparing one medium with another then *para* substituted PhP_1(pyrr) series forms a separate well-defined trend with much better correlation parameters, than the overall correlation. Using the 4-X-PhP_1(pyrr) series correlation equation parameters, we may calculate the estimated pK_α(THF) values for all bases of the P_1(pyrr) series. The difference between experimental and estimated pK_α(THF) values, which is given in the fourth column of Table S7, can be treated as a measure of relative (with respect to the 4-X-PhP_1(pyrr) series) solvation change on transfer from AN to THF. Now, taking a closer look at this difference, we may conclude that the protonated forms of 4-X-PhP_1(pyrr)

phosphazenes are in THF compared to AN by 1.2 pK_α units less stabilized by solvent, than the protonated HP_1(pyrr). Large *ortho* fragments inhibit stabilization by solvation of the protonated molecule even more. For example, compared to 4-X-PhP_1(pyrr) phosphazenes the loss is for 1-Naphthyl 0.7 pK_α units, for Cl in *ortho* position of phenyl ring from 1.3 to 2.5 pK_α units, for NO_2 in same position from 1.9 to 2.6 pK_α units.

Table S7. The pK_a(AN) and pK_α(THF) Data from Ref 6.

Compound	pK_a(AN)	pK_α(THF)	difference[a]
HP_1(pyrr)	27.01	20.8	–1.18
EtP_1(pyrr)	28.88	21.7	–0.70
t-$ButP_1$(pyrr)	28.42	20.2	0.46
4-Me_2N-$C_6H_4P_1$(pyrr)	23.88	17.3	0.00
4-MeO-$C_6H_4P_1$(pyrr)	23.12	16.8	–0.06
PhP_1(pyrr)	22.34	16.0	0.16
4-Br-$C_6H_4P_1$(pyrr)	21.19	15.4	–0.09
4-CF_3-$C_6H_4P_1$(pyrr)	20.16	14.6	–0.05
4-NO_2-$C_6H_4P_1$(pyrr)	18.51	13.3	0.05
1-$NaphtP_1$(pyrr)	20.61	14.2	0.72
2-Cl-$C_6H_4P_1$(pyrr)	20.17	13.2	1.31
2,5-Cl_2-$C_6H_3P_1$(pyrr)	18.52	11.9	1.45
2,6-Cl_2-$C_6H_3P_1$(pyrr)	18.56	11.8	1.53
2,6-Cl_2-4-NO_2-$C_6H_2P_1$(pyrr)	14.43	7.8	2.49
2-NO_2-4-Cl-$C_6H_3P_1$(pyrr)	17.68	10.8	1.92
2-NO_2-5-Cl-$C_6H_3P_1$(pyrr)	17.27	10.1	2.31
2-NO_2-4-CF_3-$C_6H_3P_1$(pyrr)	16.54	9.5	2.37
2,4-NO_2-$C_6H_3P_1$(pyrr)	14.88	8.0	2.64
2,6-NO_2-$C_6H_3P_1$(pyrr)	14.12	7.5	2.58

[a] Difference = pK_a(AN) times slope from 4-X-Ph(pyrr) series plus intercept from 4-X-Ph(pyrr) series minus pK_α(THF), this quantity measures the difference between experimental and estimated pK_α(THF) values.

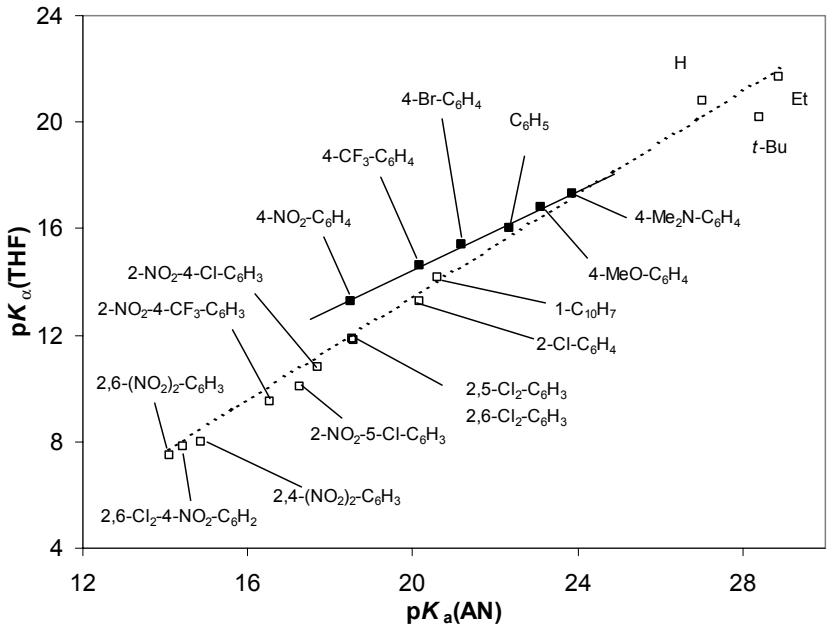


Figure S6. Correlation of the pK_a(AN) and pK_α(THF) values of P_1(pyrr) series. The solid squares and solid line corresponds to 4-X-PhP_1(pyrr) compounds, open squares and dotted line to the overall correlation. Data from ref 6.

References

1. Koppel, I. A.; Koppel, J.; Leito, I.; Koppel, I.; Mishima, M.; Yagupolskii, L. M. *J. Chem. Soc., Perkin Trans. II*, **2001**, 229–232 and references therein.
2. Mishima, M.; Mustanir; Fujio, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2009–2018.
3. Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. *J. Org. Chem*. **2002**, *67*, 1873–1881.
4. Kaljurand, I.; Rodima, T.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I.; Mishima, M. *J. Org. Chem*. **2003**, *68*, 9988–9993.
5. 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**, *50*, 127, 17656–17666.
6. Kaljurand, I; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019–1028.
7. Leito, I.; Kaljurand, I.; Koppel, I. A.; Yagupolskii, L. M.; Vlasov, V. M. *J. Org. Chem.*, **1998**, *63*, 7868–7874.

8. Kisanga, P. B.; Verkade, J. G.; Schwesinger, R. *J. Org. Chem.* **2000,** *65,* 5431–5432
9. Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data*. **1998**, *27*, 3, 413–656.
10. 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
11. Schwesinger, R., Willaredt, J., Schlemper, H., Keller, M., Schmitt,D., Fritz, H. *Chem. Ber*. **1994**, *127*, 2435–2454.
12. 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.
13. Sooväli, L.; Rodima, T.; Kaljurand, I.; Kütt, A.; Koppel I. A. and Leito. I. *Org. and Bioorg. Chem.,* **2006,** *4,* 2100–2105.
14. Raczyńska, E. D.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Gelbard, G.; Vielfaure-Joly, F. *J. Phys. Org. Chem.* **2001**, *14*, 25–34.
15. Schwesinger, R.; Missfeldt, M.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1165–1167.
16. Schwesinger, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1164–1165.
17. 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.
18. *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*; Palm, V. Ed.; VINITI: Moscow-Tartu, 1975–1985.
19. Peips, M.; Koppel, J.; Pihl, V. O.; Koppel, I. A. *Org. React.* **1976**, *13*, 203–219.
20. Burk, P.; Koppel, I. A.; Koppel, I.; Leito, I. Travnikova, O. *Chem. Phys. Lett.* **2000**, *323*, 482–489.
21. Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1.
22. Raczyńska, E. D.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Woźniak, K.; Kurg, R.; Carins, S. N. *Trends in Organic Chemistry* **1998**, *7*, 95–103.
23. Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

III

Chem. Eur. J.

Brønsted Basicities of Diamines in the Gas Phase, Acetonitrile and Tetrahydrofuran

Eva-Ingrid Rõõm, Agnes Kütt, Ivari Kaljurand, Ivar Koppel, Ivo Leito, Ilmar A. Koppel, Masaaki Mishima, Kenta Goto and Yuji Miyahara

Uncertainty of the Experimental Results and Calculations

pK_a Measurements in Acetonitrile. The uncertainty estimation of pK_a values measured according to the above-described method has been carried out recently.[1] Based on the results of that study we estimate the standard uncertainties of the obtained pK_a values if interpreted "in the framework" of the AN basicity scale (that is, uncertainties to be used when comparing the different pK_a values from the scale to each other) as 0.05 pK_a units The standard uncertainties of the absolute pK_a values "detached from the scale" (that is treating them as negative logarithms of equilibrium constants) can be estimated as 0.2 pK_a units. See ref [1] for further information.

Gas-phase basicity calculations. The average difference between the calculated and experimental results is 0.1 kcal·mol^{-1} indicating that there is no systematic under- or overestimation of basicity. The standard deviation of calculated values from experiment is s = 1.7 kcal·mol^{-1}. 70% (14 values out of 20) fall within ±1s from the experiment, 95% (19 values out of 20) fall within ±2s and all calculated values are within ±3s from the experiment. Thus the deviations are normally distributed to a very good approximation and trying to explain the deviation of any of the calculated values from the experiment would be unjustified. It is important to note that all qualitative conclusions drawn in the discussion below remain valid, irrespective whether computational or experimental data are used.

Isodesmic Reactions. In the case of **B1** the two reactions ID11 and ID13 yielded almost identical SE contributions (2.3 kcal·mol^{-1}, Table 2 in the main text), which is to be expected since the intrinsic strain of a six-member aliphatic cycle is negligible. For **B2** the SE contribution 5.3 kcal·mol^{-1} obtained using reaction ID11 is well in line with those for **B1**, keeping in mind that the additional methyl groups force the molecule into *exo-exo* conformation creating repulsion between the lone pairs. However, using for **B2** reaction ID13 leads to a meaningless SE value of -1.7 kcal·mol^{-1}. All our attempts to rerun calculations with different conformations for the reactants led to the same result.

It is important to note that the two reactions ID11 and ID13 are very different and the reaction ID13 contains altogether 8 (!) molecules. The standard deviation of the calculated basicity values from the experiment is s = 1.7 kcal·mol^{-1} (see the results section). The standard uncertainty (uncertainty at standard deviation level) of our experimental values can be roughly estimated as 0.5 kcal·mol^{-1}, consider that for every such calculation two species (neutral amine and its protonated form) are calculated assumingly with around the same uncertainties and if we assume independence of all the uncertainties then we get $0.5^2 + 2 \cdot u_{calc}^2 = 1.7^2$, from where the estimate of the uncertainty of enthalpy of a single species u_{calc} = 1.1 kcal·mol^{-1}. Now we can calculate the standard uncertainty of the enthalpy reaction Eq. ID13 (assuming that for a small ethane molecule the uncertainty is negligible compared to the others): $u_{calc}(ID13)^2 = u_{calc}^2 + (2 \cdot u_{calc})^2 + u_{calc}^2$. The calculation leads to $u_{calc}(ID13)$ = 2.7 kcal·mol^{-1}. Thus in 95% of cases the deviations should be within 5.4 kcal·mol^{-1}, which is by far sufficient to account for this case (and also others few cases found in Table 2 of the main text) where SE values are negative.

References

[1] L. Sooväli, I. Kaljurand, A. Kütt, I. Leito, *Anal. Chim. Acta.* **2006**, *566*, 290-303.

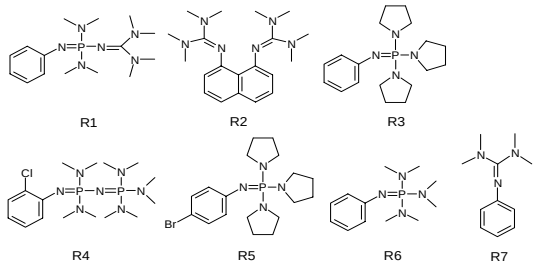
Table S1. Ionic Radii of the Protonated Forms of the Studied Bases and Indicator Phosphazene Bases and Methanesulfonate Anion.

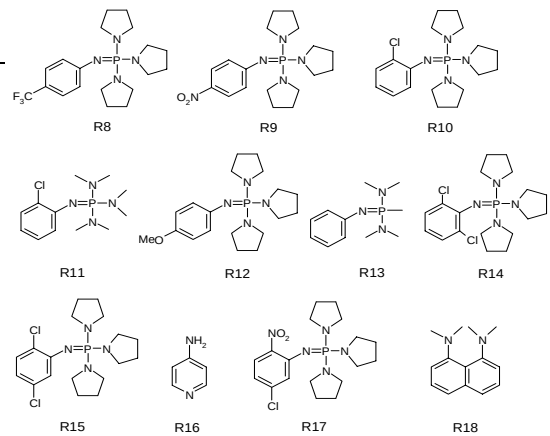
Ion	ion-pair radius, Å[a]	Ion	ion-pair radius, Å[a]
SpH^+, $R3H^+$, $R5H^+$, $R6H^+$, $R8H^+$, $R9H^+$, $R10H^+$, $R11H^+$	4.0	$M7H^+$, $B1H^+$, $B2H^+$	3.8
$R4H^+$	4.8	$D4H^+$	3.4
$D1H^+$-$D3H^+$, $D5H^+$-$D10H^+$, $M4H^+$	3.1	$Pi1H^+$, $Pi2H^+$, $P1H^+$, $P2H^+$, $P3H^+$, HpH^+	3.0
$M5H^+$	1.9	$M1H^+$, $M2H^+$, $M3H^+$	2.7
$R2H^+$	4.7	$CH_3SO_3^-$	2.5

[a] Ionic radii from previous works (a) T. Rodima, I. Kaljurand, A. Pihl, V. Mäemets, I. Leito, I. Koppel, *J. Org. Chem.* **2002**, *67*, 1873-1881; (b) I. Kaljurand, T. Rodima, A. Pihl, V. Mäemets, I. Leito, I. Koppel, M. Mishima, *J. Org. Chem.* **2003**, *68*, 9988-9993. In cases when no data were available, the radii were estimated by PM3 calculations. For explanatory definitions of bases see Schemes 1 and 2 in the main text and Table S1 and Scheme S1 in Supporting Information.

Scheme S1. Reference Indicator Bases for UV-Vis Titrations and Gas-Phase Experiments

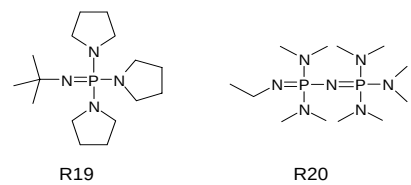
	Compound	pK_{ip}(THF)	Reference
R1	$PhP_1(TMG)dma_2$	18.13	6
R2	TMGN	16.47	6
R3	PhP_1(pyrr)	16.05	5
R4	2-Cl-$C_6H_4P_2$(dma)	15.85	5
R5	4-Br-$C_6H_4P_1$(pyrr)	15.41	5
R6	PhP_1(dma)	15.22	3
R7	PhTMG	14.98	3
R8	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	2
R9	4-NO_2-$C_6H_4P_1$(pyrr)	13.26	1
R10	2-Cl-$C_6H_4P_1$(pyrr)	13.23	5
R11	2-Cl-$C_6H_4P_1$(dma)	12.49	3
		pK_a(AN)	
R12	4-MeO-$C_6H_4P_1$(pyrr)	23.12	5
R3	PhP_1(pyrr)	22.34	5
R6	PhP_1(dma)	21.25	3
R5	4-Br-$C_6H_4P_1$(pyrr)	21.19	5
R13	$PhP_1(dma)_2Me$	21.03	4
R7	PhTMG	20.84	3
R10	2-Cl-$C_6H_4P_1$(pyrr)	20.17	5
R8	4-CF_3-$C_6H_4P_1$(pyrr)	20.16	2
R11	2-Cl-$C_6H_4P_1$(dma)	19.07	3
R14	2,6-Cl_2-$C_6H_3P_1$(pyrr)	18.56	5
R15	2,5-Cl_2-$C_6H_3P_1$(pyrr)	18.52	5
R9	4-NO_2-$C_6H_4P_1$(pyrr)	18.51	1
R16	4-NH_2-Pyridine	17.62	3
R17	2-NO_2-5-Cl-$C_6H_3P_1$(pyrr)	17.27	2
	GP	GB_{exp}	
R13	$PhP_1(dma)_2Me$	244.8	4
R7	PhTMG	244.3	3
R18	Proton sponge	238.2	2





Strong bases used as basic titrants

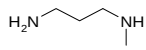
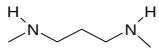
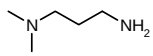
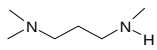
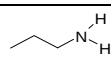
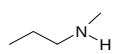
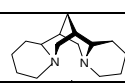
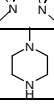
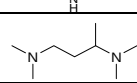
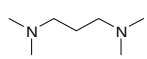
		pK_a(AN)	
R19	*t*-BuP_1(pyrr)	28.42	3
		pK_{ip}(THF)	
R20	EtP_2(dma)	24.9	2

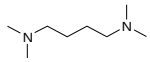
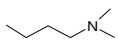
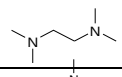


References

1. Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. *J. Org. Chem* . 2005, *70* , 1019-1028.
2. Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. *J. Org. Chem* . 2002, *67* , 1873-1881.
3. Kaljurand, I.; Rodima, T.; Leito, I.; Koppel, I.; Schwesinger, R. *J. Org. Chem* . 2000, *65* , 6202-6208.
4. Kaljurand, I.; Rodima, T.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I.; Mishima, M. *J. Org. Chem* . 2003, *68* , 9988-9993
5. Rodima, T.; Mäemets, V.; Koppel, I. *J. Chem. Soc., Perkin Trans. 1* . 2000, *16* , 2637-2644.
6. 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.

Table S2. Results of Titration Experiments in THF.

No (B)	Studied base (B)		Reference base (A)[a]	pK_{ip}(A)[a]	ΔpK_{ip}	pK_{ip}(B)[b]	pK_{ip}(B)[c]	pK_{α}(B)[c]
D8		N-Me-1,3-Diaminopropane	PhP_1(pyrr)	16.05	0.22	15.83		
			4-Br-$C_6H_4P_1$(pyrr)	15.41	-0.45	15.86	15.84	15.20
B2		N,N'-Me_2-bispidine	PhP_1(pyrr)	16.05	0.57	15.48		
			2-Cl-$C_6H_4P_2$(dma)	15.85	0.28	15.57		
			TMGN	16.47	0.88	15.59	15.55	15.43
D6		N,N`-Me_2-1,3-Diaminopropane	$PhP_1(dma)_2Me$	15.41	-0.07	15.48		
			2-Cl-$C_6H_4P_2$(dma)	15.85	0.36	15.49	15.49	14.86
D7		N,N-Me_2-1,3-diaminopropane	4-Br-$C_6H_4P_1$(pyrr)	15.41	-0.09	15.50		
			4-CF_3-$C_6H_4P_1$(pyrr)	14.57	-0.58	15.15	15.32	14.69
Hp		Homopiperazine	PhP_1(dma)	15.22	0.07	15.15		
			PhP_1(pyrr)	16.05	1.01	15.04	15.09	14.40
Pi1		Piperidine	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	-0.5	15.07		
			2-Cl-$C_6H_4P_2$(dma)	15.85	0.9	14.95	15.01	14.30
D5		N,N,N`-Me_3-1,3-Diaminopropane	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	-0.35	14.92		
			PhP_1(dma)	15.22	0.33	14.89	14.90	14.30
P1		Piperazine	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	-0.28	14.85		
			4-CF_3-$C_6H_4P_1$(pyrr)	14.57	-0.30	14.87		
			2-Cl-$C_6H_4P_1$(dma)	12.49	-2.38	14.87	14.86	14.16
M1		Propylamine	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	-0.14	14.71		
			PhP_1(dma)	15.22	0.48	14.74	14.72	13.76
M2		N-methyl-N-propylamine	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	-0.04	14.61		
			PhP_1(dma)	15.22	0.60	14.62	14.61	13.65
M5		Diisopropylamine	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	-0.04	14.61		
			PhP_1(dma)	15.22	0.64	14.58	14.59	13.63
Sp		Sparteine	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	0.3	14.27		
			PhP_1(dma)	15.22	1.03	14.19	14.23	14.26
P2		1-Me-piperazine	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	0.52	14.05		
			4-NO_2-$C_6H_4P_1$(pyrr)	13.26	-0.9	14.16	14.11	13.40
D10		N,N,N',N'-Me_4-1,3-diaminobutane	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	0.59	13.98		
			4-NO_2-$C_6H_4P_1$(pyrr)	13.26	-0.88	14.14	14.06	13.44
D3		N,N,N',N'-Me_4-1,3-diaminopropane	4-Br-$C_6H_4P_1$(pyrr)	15.41	*1.85*	13.56		
			4-CF_3-$C_6H_4P_1$(pyrr)	14.57	0.88	13.69	13.62	12.99

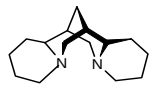
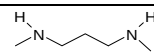
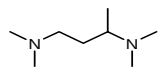
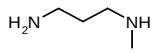
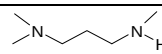
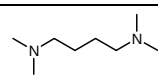
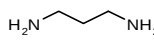
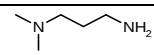
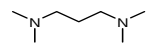
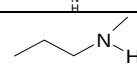
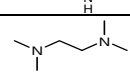
Pi2		1-Me-piperidine	4-NO_2-$C_6H_4P_1$(pyrr)	13.26	-0.45	13.71		
			4-CF_3-$C_6H_4P_1$(pyrr)	14.57	1.05	13.52	13.62	12.91
M3		N-ethyl-N,N-dimethylamine	2-Cl-$C_6H_4P_1$(pyrr)	13.23	-0.38	13.61		
			4-CF_3-$C_6H_4P_1$(pyrr)	14.57	0.98	13.59	13.60	12.62
D4		N,N,N',N'-Me_4-1,4-diaminobutane	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	1.2	13.37		
			PhP_1(dma)	15.22	1.7	13.52	13.44	13.08
M4		N-butyl-N,N-dimethylamine	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	1.1	13.47		
			2-Cl-$C_6H_4P_1$(dma)	12.49	-0.90	13.39		
			2-Cl-$C_6H_4P_1$(pyrr)	13.23	-0.17	13.40	13.42	12.80
D2		N,N,N',N'-Me_4-diaminoethane	4-CF_3-$C_6H_4P_1$(pyrr)	14.57	1.14	13.43		
			PhP_1(dma)	15.22	1.88	13.34	13.38	12.78
P3		N,N'-Me_2-piperazine	2-Cl-$C_6H_4P_1$(dma)	12.49	-0.60	13.13		
			4-NO_2-$C_6H_4P_1$(pyrr)	13.26	0.15	13.11	13.10	12.39
M7		Tripropylamine	2-Cl-$C_6H_4P_1$(pyrr)	13.23	0.09	13.14		
			4-CF_3-$C_6H_4P_1$(pyrr)	14.57	1.5	13.07	13.10	13.00

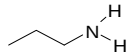
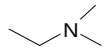
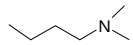
[a] Structures and pK_{ip} values of reference bases are given in Scheme S1

[b] pK_{ip} values for studied bases obtained from individual measurements

[c] Assigned pK_{ip} and pK_{α} values for studied bases

Table S3. Results of Titration Experiments in Acetonitrile.

No(B)	Studied base (B)	Reference base (A)[a]	pK_a(A)[a]	ΔpK_a	pK_a(B)[b]	pK_a(B)[c]
B2	 N,N'-Me_2-bispidine	PhP_1(pyrr)	22.34	0.41	22.75	
		4-MeO-$C_6H_4P_1$(pyrr)	23.12	-0.39	22.73	
		PhP_1(dma)	21.25	1.5	22.75	22.74
Sp	 Sparteine	PhP_1(pyrr)	22.34	-0.63	21.71	
		PhP_1(dma)	21.25	0.41	21.66	
		PhP_1(dma)	21.25	0.42	21.67	
		4-Br-$C_6H_4P_1$(pyrr)	21.19	0.49	21.68	
		$PhP_1(dma)_2Me$	21.03	0.60	21.63	
		PhTMG	20.84	0.77	21.61	21.66
B1	 Bispidine	PhP_1(pyrr)	22.34	-0.68	21.66	
		PhP_1(dma)	21.25	0.31	21.56	
		PhTMG	20.84	0.59	21.43	
		$PhP_1(dma)_2Me$	21.03	0.50	21.53	
		4-Br-$C_6H_4P_1$(pyrr)	21.19	0.39	21.58	21.55
D6	 N,N`-Me_2-1,3-Diaminopropane	4-CF_3-$C_6H_4P_1$(pyrr)	20.16	0.19	20.35	
		$PhP_1(dma)_2Me$	21.03	-0.60	20.43	20.39
D10	 N,N,N',N'-Me_4-1,3-diaminobutane	2-Cl-$C_6H_4P_1$(pyrr)	20.17	-0.04	20.13	
		4-CF_3-$C_6H_4P_1$(pyrr)	20.16	-0.09	20.07	
		4-CF_3-$C_6H_4P_1$(pyrr)	20.16	-0.10	20.06	20.09
D8	 N-Me-1,3-Diaminopropane	4-CF_3-$C_6H_4P_1$(pyrr)	20.16	-0.11	20.05	
		2-Cl-$C_6H_4P_1$(dma)	19.07	0.96	20.03	20.04
D5	 N,N,N`-Me_3-1,3-Diaminopropane	4-CF_3-$C_6H_4P_1$(pyrr)	20.16	-0.17	19.99	
		$PhP_1(dma)_2Me$	21.03	-1.00	20.03	20.01
D4	 N,N,N',N'-Me_4-1,4-diaminobutane	2-Cl-$C_6H_4P_1$(dma)	19.07	0.85	19.92	
		4-NO_2-$C_6H_4P_1$(pyrr)	18.51	1.43	19.94	
		4-CF_3-$C_6H_4P_1$(pyrr)	20.16	-0.25	19.91	19.93
D9	 1,3-diaminopropane	4-CF_3-$C_6H_4P_1$(pyrr)	20.16	-0.48	19.68	
		2-Cl-$C_6H_4P_1$(dma)	19.07	0.65	19.72	19.70
D7	 N,N'-Me_2-piperazine	4-CF_3-$C_6H_4P_1$(pyrr)	20.16	-0.54	19.62	
		2-Cl-$C_6H_4P_1$(dma)	19.07	0.45	19.52	19.57
Pi1	 Piperidine	2-Cl-$C_6H_4P_1$(dma)	19.07	0.25	19.32	
		4-CF_3-$C_6H_4P_1$(pyrr)	20.16	-0.90	19.26	19.29
D3	 N,N,N',N'-Me_4-1,3-diaminopropane	2-Cl-$C_6H_4P_1$(dma)	19.07	0.19	19.26	
		4-NO_2-$C_6H_4P_1$(pyrr)	18.51	0.77	19.28	19.27
Hp	 Homopiperazine	2-Cl-$C_6H_4P_1$(dma)	19.07	0.04	19.11	
		4-NO_2-$C_6H_4P_1$(pyrr)	18.51	0.58	19.09	19.10
M2	 N-methyl-N-propylamine	2-Cl-$C_6H_4P_1$(dma)	19.07	-0.15	18.92	
		2,5-Cl_2-PhP_1(pyrr)	18.52	0.4	18.92	18.92
M5	 Diisopropylamine	2-Cl-$C_6H_4P_1$(dma)	19.07	-0.26	18.81	
		4-NO_2-$C_6H_4P_1$(pyrr)	18.51	0.30	18.81	18.81
P1	 Piperazine	2-Cl-$C_6H_4P_1$(dma)	19.07	-0.40	18.67	
		4-NO_2-$C_6H_4P_1$(pyrr)	18.51	0.19	18.70	18.69
D2	 N,N,N',N'-Me_4-diaminoethane	2-Cl-$C_6H_4P_1$(dma)	19.07	-0.40	18.67	
		4-NO_2-$C_6H_4P_1$(pyrr)	18.51	0.18	18.69	18.68

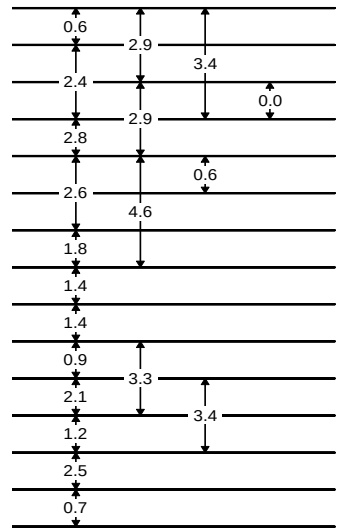
M1		Propylamine	4-NO_2-$C_6H_4P_1$(pyrr)	18.51	-0.04	18.47	
			2-Cl-$C_6H_4P_1$(dma)	19.07	-0.68	18.39	18.43
M3		N-ethyl-N,N-dimethylamine	2-Cl-$C_6H_4P_1$(dma)	19.07	-0.74	18.33	
			4-NO_2-$C_6H_4P_1$(pyrr)	18.51	-0.19	18.32	18.33
M7		Tripropylamine	2-Cl-$C_6H_4P_1$(dma)	19.07	-0.82	18.25	
			4-NO_2-$C_6H_4P_1$(pyrr)	18.51	-0.26	18.25	18.25
Pi2		1-Me-piperidine	4-NH_2-Pyridine	17.62	0.59	18.21	
			4-NO_2-$C_6H_4P_1$(pyrr)	18.51	-0.25	18.26	
			2,6-Cl_2-$C_6H_3P_1$(pyrr)	18.56	-0.29	18.27	18.25
M4		N-butyl-N,N-dimethylamine	2-Cl-$C_6H_4P_1$(dma)	19.07	-0.83	18.24	
			4-NO_2-$C_6H_4P_1$(pyrr)	18.51	-0.27	18.24	18.24
P2		1-Me-piperazine	2,5-Cl_2-$C_6H_3P_1$(pyrr)	18.52	-0.45	18.07	
			2-NO_2-5-Cl-$C_6H_3P_1$(pyrr)	17.27	0.80	18.07	18.07
P3		N,N'-Me_2-piperazine	2,5-Cl_2-$C_6H_3P_1$(pyrr)	18.52	-1.17	17.35	
			2-NO_2-5-Cl-$C_6H_3P_1$(pyrr)	17.27	0.10	17.37	17.36

[a] Structures and pK_a values of reference bases are given in Scheme S1

[b] pK_a values for studied bases obtained from individual measurements

[c] Assigned pK_a values for studied bases

Table S4. Experimental Results of Gas-Phase Basicity Measurements and Calculations.

No[a]	Base	Directly measured $\Delta\Delta G_b$[b]	GB_{exp}	GB_{exp}[c]	GB_{calc}
R13	$PhP_1(dma)_2Me$		243.9	243.7[d]	242.9
Sp	(-)Sparteine		243.4		240.8
B2	N,N'-Me_2-Bispidine		240.8		238.5
R7	PhTMG		240.6	240.4	240.6
D4	N,N,N',N'-Me_4-1,3-diaminobutane		237.9		236.7
R18	Proton sponge		237.3	238.0	239.2
D3	N,N,N',N'-Me_4-1,3-diaminopropane		235.2	235.5	234.8
D5	N,N,N'-Me_3-1,3-diaminopropane		233.3		234.7
D7	N,N-Me_2-1,3-diaminopropane		231.9	233.1	234.2
D2	N,N,N',N'-Me_4-diaminoethane		230.5	232.0	231.2
M7	Tri-*n*-propylamine		229.5[e]	229.5	229.0
D8	N-Me-1,3-diaminopropane		227.3		231.4
M6	Triethylamine		226.1	227.0	228.2
Hp	Homopiperazine		223.6		225.0
M5	Diisopropylamine		222.9	224.3	222.1

[a] Structures of compouds are given in Schemes 1, 2 and S1.

[b] Experimental $\Delta\Delta G_b$ values from this work.

[c] Hunter, P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413-656.

[d] Kaljurand, I.; Koppel, I.A.; Kütt, A.; Rõõm, E.-I.; Rodima, T.; Koppel, I.; Mishima, M.; Leito, I. Experimental Gas-Phase Basicity Scale of Superbasic Phosphazenes *J. Phys. Chem. A*, accepted on December 5, 2006. DOI: 10.1021/jp066182m

[e] The scale is anchored to tripropylamine, its value taken from Hunter et al[c]

Table S5. Results of calculations of gas-phase energies of diamines, amines and hydrocarbons at DFT B3LYP/6-311+G level**

No(ID)[a]	No[b]	Compounds	[(DAH$^+_{HB}$) - (DAH$^+_{NHB}$)] ΔH[c] kcal·mol^{-1}	ΔG[d] kcal·mol^{-1}	Neutral *E* AU	Neutral *H* AU	Neutral *G* AU	Protonated Form Geometry	Protonated Form *E* AU	Protonated Form *H* AU	Protonated Form *G* AU	*GB* kcal·mol^{-1}	*PA* kcal·mol^{-1}
		Diamines											
1	D1	**$Me_2NCH_2NMe_2$**			-308.5242	-308.3212	-308.3664		-308.9106	-308.6918	-308.7371	226.3	234.0
2	D2	**$Me_2N(CH_2)_2NMe_2$**			-347.8447	-347.6119	-347.6599	HB	-348.2406	-347.9921	-348.0384	231.2	240.1
								NHB	-348.2266	-347.9779	-348.0258		
		Best[e]	-8.9	-7.9	-347.8447	-347.6119	-347.6599		-348.2406	-347.9921	-348.0384	231.2	240.1
3	D3	**$Me_2N(CH_2)_3NMe_2$**			-387.1716	-386.9090	-386.9597	HB	-387.5733	-387.2955	-387.3439	234.8	244.0
								NHB	-387.5524	-387.2739	-387.3259		
		Best[e]	-13.5	-11.3	-387.1716	-386.9090	-386.9597		-387.5733	-387.2955	-387.3439	234.8	244.0
4	D4	**$Me_2N(CH_2)_4NMe_2$**			-426.4963	-426.2041	-426.2587	HB	-426.9018	-426.5945	-426.6454	236.4	246.5
								NHB	-426.8755	-426.5671	-426.6223		
		Best[e]	-17.2	-14.5	-426.4963	-426.2041	-426.2587		-426.9018	-426.5945	-426.6454	236.4	246.5
5	D5	**$Me_2N(CH_2)_3NHMe$**			-347.8559	-347.6222	-347.6702	HB	-348.2578	-348.0084	-348.0542	234.7	243.8
								NHB	-348.2362	-347.9865	-348.0355		
		Best[e]	-13.7	-11.8	-347.8559	-347.6222	-347.6702		-348.2578	-348.0084	-348.0542	234.7	243.8
6	D6	**$MeNH(CH_2)_3NHMe$**			-308.5406	-308.3358	-308.3810	NHB	-308.9140	-308.6935	-308.7395	218.7	225.9
								HB	-308.9366	-308.7166	-308.7594	231.2	240.4
		Best[e]	-14.5	-12.5	-308.5406	-308.3358	-308.3810		-308.9366	-308.7166	-308.7594	231.2	240.4
7	D7	**$Me_2N(CH_2)_3NH_2$**			-308.5409	-308.3364	-308.3809	HB	-308.9422	-308.7219	-308.7642	234.2	243.4
								NHB	-308.9210	-308.7007	-308.7458		
		Best[e]	-13.3	-11.5	-308.5409	-308.3364	-308.3809		-308.9422	-308.7219	-308.7642	234.2	243.4
8	D8	**$MeNH(CH_2)_3NH_2$**						NHB	-269.5989	-269.4076	-269.4500	219.1	226.4
					-269.2248	-269.0492	-269.0909	HB	-269.6213	-269.4302	-269.4697	231.4	240.6
		Best[e]	-14.2	-12.4	-269.2248	-269.0492	-269.0909		-269.6213	-269.4302	-269.4697	231.4	240.6
9	D9	**$H_2N(CH_2)_3NH_2$**			-229.9094	-229.7630	-229.8011	HB	-230.2979	-230.1369	-230.1727	226.9	236.1
								NHB	-230.2729	-230.1113	-230.1499	212.6	220.0
		Best[e]	-16.1	-14.3	-229.9094	-229.7630	-229.8011		-230.2979	-230.1369	-230.1727	226.9	236.1
10	D10	**$Me_2NCH(CH_3)(CH_2)_2NMe_2$**			-426.4948	-426.2031	-426.2567	HB	-426.9000	-426.5928	-426.6439	236.7	246.0
								NHB	-426.8778	-426.5701	-426.6245		
		Best[e]	-14.2	-12.2	-426.4948	-426.2031	-426.2567		-426.9000	-426.5928	-426.6439	236.7	246.0
11	B1	**Bispidine**			-384.7720	-384.5513	-384.5906		-385.1684	-384.9325	-384.9714	232.7	240.7
		Best[e]			-384.7720	-384.5513	-384.5906		-385.1684	-384.9325	-384.9714	232.7	240.7
11A	O1	**1,5-Diazacyclooctane**			-346.6474	-346.4345	-346.4764		-347.0423	-346.8136	-346.8538	233.6	241.7
		Best[e]			-346.6474	-346.4345	-346.4764		-347.0423	-346.8136	-346.8538	230.5	239.3

12	B2	**N,N'Me$_2$ bispidine**			-463.4036	-463.1263	-463.1722		-463.8106	-463.5171	-463.5623	238.5	246.7
		Best[e]			-463.4036	-463.1263	-463.1722		-463.8106	-463.5171	-463.5623	238.5	246.7
12A	O2	**N,N'-diMe-1,5-Diazacyclooctane**			-425.2754	-425.0048	-425.0530		-425.6806	-425.3939	-425.4403	236.8	245.6
		Best[e]	-11.2	-10.2	-425.2754	-425.0048	-425.0530		-425.6806	-425.3939	-425.4403	236.8	245.6
13	Sp	**Sparteine**			-696.9400	-696.5276	-696.5822		-697.3506	-696.9223	-696.9760	240.8	249.2
		Best[e]			-696.9400	-696.5276	-696.5822		-697.3506	-696.9223	-696.9760	240.8	249.2
14	Hp	**Homopiperazine**			-307.3271	-307.1437	-307.1822	HB	-307.7120	-307.5129	-307.5507	225.0	233.2
					-307.3267	-307.1434	-307.1818	NHB	-307.7046	-307.5057	-307.5443	225.2	233.3
		Best[e]	-4.5	-4.0	-307.3271	-307.1437	-307.1822		-307.7120	-307.5129	-307.5507	225.0	233.2
15	P1	**Piperazine**			-268.0096	-267.8560	-267.8904	NHB	-268.3826	-268.2138	-268.2491	218.8	226.0
									-268.3799	-268.2105	-268.2465	217.2	223.9
		Best[e]	2.1	1.6	-268.0096	-267.8560	-267.8904		-268.3826	-268.2138	-268.2491	218.8	226.0
16	P2	**N-Mepiperazine**			-307.3308	-307.1482	-307.1863	NHB	-307.7112	-307.5132	-307.5516	223.0	230.5
								HB	-307.7046	-307.5061	-307.5452	219.0	226.0
		Best[e]	4.5	4.0	-307.3308	-307.1482	-307.1863		-307.7112	-307.5132	-307.5516	223.0	230.5
17	P3	**N,N'-Me$_2$piperazine**			-346.6359	-346.4248	-346.4662	NHB	-347.0233	-346.7966	-346.8382	227.2	234.8
								HB	-347.0234	-346.7960	-346.8383	227.2	234.8
		Best[e]	0.4	-0.1	-346.6359	-346.4248	-346.4662		-347.0233	-346.7966	-346.8382	227.2	234.8
		Monoamines											
18		**Me$_2$NCH$_3$**			-174.5277	-174.4016	-174.4354		-174.9012	-174.7591	-174.7933	218.3	225.8
19	M3	**Me$_2$NC$_2$H$_5$**			-213.8527	-213.6969	-213.7342		-214.2307	-214.0591	-214.0971	221.4	228.8
20		**Me$_2$NC$_3$H$_7$**			-253.1766	-252.9911	-253.0322		-253.5564	-253.3550	-253.3967	222.5	229.8
21	M4	**Me$_2$NC$_4$H$_9$**			-292.5009	-292.2857	-292.3305		-292.8817	-292.6505	-292.6955	222.8	230.4
	M5	**iPr$_2$NH**			-292.5145	-292.2998	-292.3444		-292.8935	-292.6633	-292.7083	222.1	229.6
	M6	**Et$_3$N**			-292.4972	-292.2822	-292.3268		-292.8866	-292.6557	-292.7004	228.2	235.9
	M7	**Pr$_3$N**			-410.4716	-410.1672	-410.2227		-410.8628	-410.5423	-410.5976	229.0	236.9
22	M2	**PrMeNH**			-213.8610	-213.7044	-213.7428		-214.2343	-214.0620	-214.1005	218.2	225.9
23	M1	**PrNH$_2$**			-174.5460	-174.4182	-174.4529		-174.9083	-174.7656	-174.8005	211.8	219.5
24		**Me$_2$NCH(Me)(Et)**			-292.4962	-292.2814	-292.3257		-292.8801	-292.6464	-292.6945	225.1	230.5
25	Pi8	**Piperidine**			-251.9788	-251.8138	-251.8490		-252.3554	-252.1748	-252.2103	220.4	228.0
26	Pi9	**N-Mepiperidine**			-291.2974	-291.1037	-291.1420		-291.6798	-291.4702	-291.5089	224.0	231.5
27		**Quinolizine**			-408.0669	-407.8061	-407.8490		-408.4566	-408.1800	-408.2232	228.5	236.1
28		**HNEt$_2$**			-213.8641	-213.7076	-213.7457		-214.2398	-214.0678	-214.1056	219.6	227.5
29		**Et(NH)Pr**			-253.1882	-253.0020	-253.0438		-253.5659	-253.3639	-253.4061	221.1	228.6
30		**MeNEt$_2$**			-253.1773	-252.9919	-253.0331		-253.5596	-253.3583	-253.3999	223.9	231.4
37		**Me-N(Et)-Pr**			-292.5011	-292.2859	-292.3308		-292.8850	-292.6541	-292.6995	225.1	232.5
39		**Azacyclooctane**			-330.6123	-330.3879	-330.4299		-330.9905	-330.7506	-330.7933	221.8	229.1

	Hydrocarbons								
31	**CH_4**	-40.5339	-40.4856	-40.5091					
32	**CH_3CH_3**	-79.8565	-79.7778	-79.8054					
33	***n*-C_3H_8**	-119.1811	-119.0727	-119.1032					
34	***n*-C_4H_{10}**	-158.5055	-158.3674	-158.4015					
35	**Cyclopentane**	-196.6117	-196.4655	-196.5011					
36	**Cyclohexane**	-235.9448	-235.7686	-235.8040					
38	**Cyclooctane**	-314.5753	-314.3397	-314.3829					
40	**2,4-Dimethylpentane**	-276.4771	-276.2510	-276.2957					
	Reference Compounds								
R7	**PhTMG**	-593.8014	-593.5187	-593.5763	-594.2098	-593.9122	-593.9697	240.6	248.4
R13	**$PhP_1(dma)_2Me$**	-937.0049	-936.6867	-936.7517	-937.4162	-937.0986	-937.1488	242.9	259.9
R18	**Proton sponge**	-653.9755	-653.6677	-653.7237	-654.3793	-654.0577	-654.1149	239.2	246.2

[a] Numeric identifier of compound in Table S6 of isodesmic reactions

[b] Structures of compounds are given in Schemes 1, 2 and S1.

[c] Energetic difference of entalpies in diamine (most stable) hydrogen bonded (HB) and (most stable) nonhydrogen bonded (NHB) form

[d] Energetic difference of Gibbs free energies in diamine (most stable) hydrogen bonded (HB) and (most stable) nonhydrogen bonded (NHB) form

[e] If several conformations were considered for the neutral or the protonated form then green rows marked with "Best" contain the data for the most stable conformations.
1 AU = 627.5 kcal mol^{-1}

Table S6. Treatment of Diamine Basicities Using Isodesmic Reactions,[a] Using Calculations at DFT B3LYP 6-311+G Level.**

Reactants						Products						*H*											*G*				
No(ID)[b]	No[c]	DA	n	HC_1		No(ID)[b]	No[c]	m	MA or HC_2	DA	DAH^+	MA	MAH^+	HC	*PA* (DA)	*PA* (MA)	*PA* (DA) - *PA* (MA_1)	*SE* (DA)	[*HB* +*SE* (DAH^+)]	*H* ($DAH^+$$_{im}$) - *H* ($DAH^+$$_{sym}$)	*HB* (DAH^+)	*SE* (DAH^+)	DA	DAH^+	MA	MAH^+	HC
										AU[d]	AU	AU	AU	AU	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	AU	AU	AU	AU	AU
1	D1	$Me_2NCH_2NMe_2$	3	1 CH_4		18		2	NMe_3	-308.3	-308.7	-174.4	-174.8	-40.5	234.0	225.8	8.2	-2.3	-10.5		49.95	-60.43	-308.4	-308.7	-174.4	-174.8	-40.5
2	D2	$Me_2N(CH_2)_2NMe_2$	3	2 H_3CCH_3		19	M3	2	Me_2NEt	-347.6	-348.0	-213.7	-214.1	-79.8	240.1	228.8	11.3	2.6	-8.7	-8.9	-10.92	2.20	-347.7	-348.0	-213.7	-214.1	-79.8
3	D3	$Me_2N(CH_2)_3NMe_2$	3	1 $CH_3CH_2CH_3$		20		2	Me_2NPr	-386.9	-387.3	-253.0	-253.4	-119.1	244.0	229.8	14.2	0.4	-13.8	-13.5	-21.01	7.17	-387.0	-387.3	-253.0	-253.4	-119.1
4	D4	$Me_2N(CH_2)_4NMe_2$	3	4 $CH_3(CH_2)_2CH_3$		21	M4	2	Me_2NBu	-426.2	-426.6	-292.3	-292.7	-158.4	246.5	230.4	16.1	-0.1	-16.1	-17.2	-25.25	9.12	-426.3	-426.6	-292.3	-292.7	-158.4
3	D3	$Me_2N(CH_2)_3NMe_2$	3	1 $CH_3CH_2CH_3$		20		2	Me_2NPr	-386.9	-387.3	-253.0	-253.4	-119.1	244.0	229.8	14.2	0.4	-13.8	-13.5	-21.01	7.17	-387.0	-387.3	-253.0	-253.4	-119.1
5	D5	$Me_2N(CH_2)_3NHMe$	3	1 $CH_3CH_2CH_3$		20		1	Me_2NPr	-347.6	-348.0	-253.0	-253.4	-119.1	243.8	229.8	14.0	0.4	-13.6	-13.7	-20.27	6.65	-347.7	-348.1	-253.0	-253.4	-119.1
						22	M2	1	MeHNPr			-213.7	-214.1			225.9									-213.7	-214.1	
6	D6	$MeHN(CH_2)_3NHMe$	3	1 $CH_3CH_2CH_3$		22	M2	2	MeHNPr	-308.3	-308.7	-213.7	-214.1	-119.1	240.4	225.9	14.6	0.2	-14.4	-14.5	-23.13	8.76	-308.4	-308.8	-213.7	-214.1	-119.1
7	D7	$Me_2N(CH_2)_3NH_2$	3	1 $CH_3CH_2CH_3$		23	M1	1	H_2NPr	-308.3	-308.7	-174.4	-174.8	-119.1	243.4	219.5		0.2	-13.4	-13.3	-18.69	5.26	-308.4	-308.8	-174.5	-174.8	-119.1
						20		1	Me_2NPr			-253.0	-253.4			229.8	13.6								-253.0	-253.4	
8	D8	$H_2N(CH_2)_3NHMe$	3	1 $CH_3CH_2CH_3$		22	M2	1	MeHNPr	-269.0	-269.4	-213.7	-214.1	-119.1	240.6	225.9	14.7	0.4	-14.2	-14.2	-20.67	6.42	-269.1	-269.5	-213.7	-214.1	-119.1
						23	M1	1	H_2NPr			-174.4	-174.8			219.5									-174.5	-174.8	
9	D9	$H_2N(CH_2)_3NH_2$	3	1 $CH_3CH_2CH_3$		23	M1	2	H_2NPr	-229.8	-230.1	-174.4	-174.8	-119.1	236.1	219.5	16.6	0.4	-16.2	-16.1	-24.75	8.56	-229.8	-230.2	-174.5	-174.8	-119.1
10	D10	$Me_2NCH(CH_3)$ $(CH_2)_2NMe_2$	3	1 $CH_3CH_2CH_3$		20		1	Me_2NPr $Me_2NCH(CH_3)$	-426.2	-426.6	-253.0	-253.4	-119.1	246.0	229.8		-2.0	-17.5	-14.2	-21.10	3.56	-426.3	-426.6	-253.0	-253.4	-119.1
						24		1	CH_3CH_3			-292.3	-292.6			230.5	15.5								-292.3	-292.7	
11	B1	Bispidine	3	1 $CH_3CH_2CH_3$		25	Pi1	2	Piperidine	-384.6	-384.9	-251.8	-252.2	-119.1	240.7	228.0	12.7	2.3	-10.4		-17.23	6.82	-384.6	-385.0	-251.8	-252.2	-119.1
		Bispidine	3	2 H_3CCH_3		28		2	$HNEt_2$	-384.6	-384.9	-213.7	-214.1	-79.8	240.7	227.5	13.2	2.3	-10.9		-17.23	6.36	-384.6	-385.0	-213.7	-214.1	-79.8
						40		1	2,4-Me_2-pentane					-276.3													-276.3
12	B2	N,N'-Me_2-bispidine	3	1 $CH_3CH_2CH_3$		26	Pi2	2	Me-piperidine	-463.1	-463.5	-291.1	-291.5	-119.1	246.7	231.5	15.2	5.3	-10.0		-17.15	7.17	-463.2	-463.6	-291.1	-291.5	-119.1
		N,N'-Me_2-bispidine	3	4 H_3CCH_3		30		2	$MeNEt_2$	-463.1	-463.5	-253.0	-253.4	-79.8	246.7	231.4	15.3	-1.7	-17.1		-17.15	0.09	-463.2	-463.6	-253.0	-253.4	-79.8
						40		1	2,4-Me_2-pentane					-276.3													-276.3
13	Sp	Sparteine	3	1 $CH_3CH_2CH_3$		27		2	Octahydro-2H-quinolizin	-696.5	-696.9	-407.8	-408.2	-119.1	249.2	236.1	13.1	7.5	-5.6		-16.38	10.80	-696.6	-697.0	-407.8	-408.2	-119.1
14	Hp	Homopiperazine	3	1 Cyclopentane		25	Pi1	2	Piperidine	-307.1	-307.5	-251.8	-252.2	-196.5	233.2	228.0	5.1	11.5	6.4	-4.5			-307.2	-307.6	-251.8	-252.2	-196.5
		Homopiperazine	3	2 H_3CCH_3		28		1	$HNEt_2$	-307.1	-307.5	-213.7	-214.1	-79.8	233.2	227.5		6.5	1.9	-4.5	-7.10	8.98	-307.2	-307.6	-213.7	-214.1	-79.8
						29		1	Et(NH)Pr			-253.0	-253.4			228.6	4.6								-253.0	-253.4	
15	Pi	Piperazin chair	3	1 Cyclohexane		25	Pi1	2	Piperidine	-267.9	-268.2	-251.8	-252.2	-235.8	226.0	228.0	-2.0	1.9	3.9				-267.9	-268.2	-251.8	-252.2	-235.8
		Piperazin chair	3	2 H_3CCH_3		28		2	$HNEt_2$	-267.9	-268.2	-213.7	-214.1	-79.8	226.0	227.5	-1.5	2.3	3.8	-2.1	2.07	1.70	-267.9	-268.2	-213.7	-214.1	-79.8
		Piperazin boat	3	1 Cyclohexane		25	Pi1	2	Piperidine	-267.9	-268.2	-251.8	-252.2	-235.8	223.9	228.0	-4.1	1.9	6.0				-267.9	-268.2	-251.8	-252.2	-235.8
		Piperazin boat	3	2 H_3CCH_3		28		2	$HNEt_2$	-267.9	-268.2	-213.7	-214.1	-79.8	223.9	227.5	-3.6	2.3	5.9	-2.1	2.07	3.79	-267.9	-268.2	-213.7	-214.1	-79.8
16	P2	N-Me-piperazine chair	3	1 Cyclohexane		25	Pi1	1	Piperidine	-307.1	-307.5	-251.8	-252.2	-235.8	230.5	228.0		0.4	1.4	-4.5			-307.2	-307.6	-251.8	-252.2	-235.8
						26	Pi2	1	Mepiperidine			-291.1	-291.5			231.5	-0.9								-291.1	-291.5	
		N-Me-piperazine chair	3	2 H_3CCH_3		30		1	$MeNEt_2$	-307.1	-307.5	-253.0	-253.4	-79.8	230.5	231.4	-0.9	-2.7	-1.8	-4.5	2.16	-4.00	-307.2	-307.6	-253.0	-253.4	-79.8
						28		1	$HNEt_2$			-213.7	-214.1			227.5									-213.7	-214.1	
		N-Me-piperazine boat	3	1		25	Pi1	1	Piperidine	-307.1	-307.5	-251.8	-252.2	-235.8	226.0	228.0		0.4	5.9	-4.5	2.16	3.71	-307.2	-307.5	-251.8	-252.2	-235.8
						26	Pi2	1	Me-piperidine			-291.1	-291.5			231.5	-5.4								-291.1	-291.5	
		N-Me-piperazine boat	3	2 H_3CCH_3		30		1	$MeNEt_2$	-307.1	-307.5	-253.0	-253.4	-79.8	226.0	231.4	-5.3	-2.7	2.6	-4.5	2.16	0.49	-307.2	-307.5	-253.0	-253.4	-79.8
						28		1	$HNEt_2$			-213.7	-214.1			227.5									-213.7	-214.1	
17	P3	N,N'-Me_2-piperazine chair	3	1 Cyclohexane		26	Pi2	2	Me-piperidine	-346.4	-346.8	-291.1	-291.5	-235.8	234.8	231.5	3.3	8.8	5.5	-0.4			-346.5	-346.8	-291.1	-291.5	-235.8
		N,N'-Me_2-piperazine chair	3	2 H_3CCH_3		30		2	$MeNEt_2$	-346.4	-346.8	-253.0	-253.4	-79.8	234.8	231.4	3.4	2.1	-1.3	-0.4	-0.18	-1.10	-346.5	-346.8	-253.0	-253.4	-79.8
		N,N'-Me_2-piperazine boat	3	1 Cyclohexane		26	Pi2	2	Me-piperidine	-346.4	-346.8	-291.1	-291.5	-235.8	234.4	231.5	2.9	8.8	5.8	-0.4	-0.18	6.01	-346.5	-346.8	-291.1	-291.5	-235.8
		N,N'-Me_2-piperazine boat	3	2 H_3CCH_3		30		2	$MeNEt_2$	-346.4	-346.8	-253.0	-253.4	-79.8	234.4	231.4	3.0	2.1	-0.9	-0.4	-0.18	-0.73	-346.5	-346.8	-253.0	-253.4	-79.8
11A	O1	1,5-diazacyclooctane	3	2 H_3CCH_3		29		2	Et(NH)Pr	-346.4	-346.8	-253.0	-253.4	-79.8	239.3	228.6	10.8	8.7	-2.1		-18.14	16.07	-346.5	-346.9	-253.0	-253.4	-79.8
		1,5-diazacyclooctane	3	1 Cyclooctane		39		2	Azacyclooctane	-346.4	-346.8	-330.4	-330.8	-314.3	239.3	229.1	10.3	1.0	-9.3		-18.14	8.85	-346.5	-346.9	-330.4	-330.8	-314.4
12A	O2	N,N'-Me_2-1,5-diazacyclooctane	3	2 H_3CCH_3		37		2	Et(NMe)Pr	-425.0	-425.4	-292.3	-292.7	-79.8	245.6	232.5	13.1	7.2	-6.0	-11.2	-18.07	12.11	-425.1	-425.4	-292.3	-292.7	-79.8

[a] The exact isodesmic reactions are given in Scheme 3 in main text. Schematically:

$DA + n \cdot HC_1 = m \cdot MA_1 \; (+ m \cdot MA_2) \; (+ HC_2)$

$DAH^+ + n \cdot HC_1 = MA_1H^+ + MA_2 \; (+ HC_2)$

Denotions: DA - diamine, MA - monoamine, HC - hydrocrbon respectively

When several calculation were made for the same compound, the ones with the blue name are considered reliable and are used in discussion

[b] Numeric identifier of compound in isodesmic reactions.

[c] Structures of compouds are given in Schemes 1, 2 and S1.

[d] 1 AU = 627.5 kcal mol^{-1}

											S						
GB (DA) kcal mol^{-1}	*GB* (MA) kcal mol^{-1}	*GB* (DA) - *GB* (MA$_1$) kcal mol^{-1}	*SE* (DA) kcal mol^{-1}	[*HB* +*SE* (DAH$^+$)] kcal mol^{-1}	*G* (DAH$^+_{big}$) - *G* (DAH$^+_{conf}$) kcal mol^{-1}	*HB* (DAH$^+$) kcal mol^{-1}	*SE* (DAH$^+$) kcal mol^{-1}	HB_{length} (DAH$^+$) Å	α(N$^+$-H···N) deg	DA AU	DAH$^+$ AU	MA AU	MAH$^+$ AU	HC AU	Δ*S* (deprotonation, DA) cal (K mol)$^{-1}$	Δ*S* (deprotonation, MA)
226.3	218.3	8.0	-2.9	-11.0		49.95	-60.93	2.57	72.14	0.000152	0.000152	0.000113	0.000115	0.000079	25.80	25.17
231.2	221.4	9.8	1.9	-7.8	-7.9	-10.92	3.07	1.93	125.75	0.000161	0.000155	0.000125	0.000128	0.000093	29.59	24.54
234.8	222.5	12.4	0.9	-11.4	-11.3	-21.01	9.58	1.73	153.62	0.000170	0.000162	0.000138	0.000140	0.000102	30.86	24.65
236.4	222.8	13.6	0.5	-13.1	-14.5	-25.25	12.13	1.64	170.54	0.000183	0.000171	0.000150	0.000151	0.000114	33.81	25.59
234.8	222.5	12.4	0.9	-11.4	-11.3	-21.01	9.58	1.73	153.62	0.000170	0.000162	0.000138	0.000140	0.000102	30.86	24.65
234.7	222.5	12.2	1.0	-11.2	-11.8	-20.27	9.04	1.79	150.10	0.000161	0.000154	0.000138	0.000140	0.000102	30.65	24.65
	218.2											0.000129	0.000129			
231.2	218.2	13.0	0.9	-12.1	-12.5	-23.13	11.02	1.71	150.92	0.000152	0.000144	0.000129	0.000129	0.000102	31.07	25.80
234.2	211.8		0.6	-11.2	-11.5	-18.69	7.52	1.79	150.10	0.000149	0.000142	0.000116	0.000117	0.000102	30.65	25.59
	222.5	11.8										0.000138	0.000140			
231.4	218.2	13.2	1.0	-12.2	-12.4	-20.67	8.43	1.76	148.24	0.000140	0.000133	0.000129	0.000129	0.000102	30.65	25.80
	211.8											0.000116	0.000117			
226.9	211.8	15.1	0.9	-14.1	-14.3	-24.75	10.63	1.68	149.43	0.000128	0.000120	0.000116	0.000117	0.000102	30.86	25.59
236.7	222.5		-1.3	-12.8	-12.2	-21.10	8.30	1.72	155.60	0.000180	0.000171	0.000138	0.000140	0.000102	31.28	24.65
	225.1	11.5										0.000149	0.000161			
232.7	220.4	12.3	2.6	-9.6		-17.23	7.61	1.84	130.09	0.000132	0.000131	0.000118	0.000119	0.000102	26.74	25.38
232.7	219.6	13.1	-15.8	-28.9		-17.23	-11.66	1.84	130.09	0.000132	0.000131	0.000128	0.000127	0.000093	26.74	26.65
														0.000150		
238.5	224.0	14.6	5.4	-9.2		-17.15	7.99	1.83	134.38	0.000154	0.000152	0.000129	0.000130	0.000102	27.49	25.17
238.5	223.9	14.6	-20.1	-34.7		-17.15	-17.52	1.83	134.38	0.000154	0.000152	0.000138	0.000140	0.000093	27.49	25.10
														0.000150		
240.8	228.5	12.3	7.9	-4.4		-16.38	11.99	1.88	132.67	0.000183	0.000180	0.000144	0.000145	0.000102	27.91	25.38
225.0	220.4	4.5	9.2	4.7	-4.0					0.000129	0.000127	0.000118	0.000119	0.000119	27.49	25.38
225.0	219.6		-2.2	-6.1		-7.10	1.01	1.96	110.70	0.000129	0.000127	0.000128	0.000127	0.000093	27.49	26.65
	221.1	3.9										0.000140	0.000142			
218.8	220.4	-1.6	2.3	3.9						0.000115	0.000118	0.000118	0.000119	0.000119	24.12	25.38
218.8	219.6	-0.8	-6.1	-5.4	-1.6	2.07	-7.46	2.34	85.85	0.000115	0.000118	0.000128	0.000127	0.000093	24.12	26.65
217.2	220.4	-3.3	2.3	5.5						0.000115	0.000121	0.000118	0.000119	0.000119	22.62	25.38
217.2	219.6	-2.4	-6.1	-3.8	-1.6	2.07	-5.82	2.34	85.85	0.000115	0.000121	0.000128	0.000127	0.000093	22.62	26.65
223.0	220.4		0.4	1.4	-4.0					0.000128	0.000129	0.000118	0.000119	0.000119	25.38	25.38
	224.0	-1.0										0.000129	0.000130			
223.0	223.9	-0.9	-11.5	-10.6	-4.0	2.16	-12.72	2.29	90.24	0.000128	0.000129	0.000138	0.000140	0.000093	25.38	25.10
	219.6											0.000128	0.000127			
219.0	220.4		0.4	5.4	-4.0	2.16	3.28	2.29	90.24	0.000128	0.000132	0.000118	0.000119	0.000119	23.72	25.38
	224.0	-5.0										0.000129	0.000130			
219.0	223.9	-4.9	-11.5	-6.6	-4.0	2.16	-8.73	2.29	90.24	0.000128	0.000132	0.000138	0.000140	0.000093	23.72	25.10
	219.6											0.000128	0.000127			
227.2	224.0	3.2	8.7	5.5	0.1					0.000139	0.000140	0.000129	0.000130	0.000119	25.59	25.17
227.2	223.9	3.3	-6.8	-10.1	0.1	-0.18	-9.90	2.32	90.39	0.000139	0.000140	0.000138	0.000140	0.000093	25.59	25.10
227.2	224.0	3.3	8.7	5.4	0.1	-0.18	5.57	2.32	90.39	0.000139	0.000142	0.000129	0.000130	0.000119	24.12	25.17
227.2	223.9	3.3	-6.8	-10.1	0.1	-0.18	-9.96	2.32	90.39	0.000139	0.000142	0.000138	0.000140	0.000093	24.12	25.10
230.5	221.1	9.5	0.3	-9.2		-18.14	8.92			0.000140	0.000135	0.000140	0.000142	0.000093	29.52	25.17
230.5	229.5	1.0	0.4	-8.4		-18.14	9.71	1.74	134.17	0.000140	0.000135	0.000141	0.000143	0.000145	29.52	24.59
236.8	225.1	11.7	-1.4	-13.1	-10.2	-18.07	5.02	1.73	138.55	0.000162	0.000156	0.000151	0.000152	0.000093	29.74	24.96

Table S7. Calculations of hydrogen bond properties.

No(ID)[a]	No[b]	Complex[c]	E(Complex)	E(HD)	E(HA)	E(HB)	E(HB)[d]	Length	Angle
			AU	AU	AU	AU	kcal/mol	Å	deg
1	D1	a	-270.7022	-135.5750	-135.2067	0.0796	49.95	2.570	72.14
2	D2	a	-270.7988	-135.5732	-135.2082	-0.0174	-10.92	1.930	125.75
3	D3	a	-270.8142	-135.5726	-135.2081	-0.0335	-21.01	1.730	153.62
		d	*-349.3182*	*-174.8957*	*-174.5241*	*0.1016*	*63.74*		
4	D4	a	-270.8190	-135.5709	-135.2079	-0.0402	-25.25	1.639	170.54
		b	*-310.1356*	*-135.5709*	*-174.5243*	*-0.0404*	*-25.35*		
		c	*-310.1394*	*-174.8949*	*-135.2079*	*-0.0366*	*-22.97*		
		d	*-349.4532*	*-174.8949*	*-174.5243*	*-0.0340*	*-21.32*		
5	D5	g	-231.4984	-135.5730	-95.8931	-0.0323	-20.27	1.750	151.76
6	D6	e chair	-192.1754	-96.2456	-95.8930	-0.0369	-23.13	1.709	150.92
		e boat	*-192.1756*	*-96.2453*	*-95.8930*	*-0.0373*	*-23.38*	*1.699*	*152.34*
7	D7	h chair	-192.1856	-135.5736	-56.5822	-0.0298	-18.69	1.785	150.10
		h boat	*-192.1823*	*-135.5736*	*-56.5822*	*-0.0265*	*-16.63*	*1.857*	*142.03*
8	D8	f chair	-152.8617	-96.2466	-56.5822	-0.0329	-20.67	1.762	148.24
		f boat	*-152.8579*	*-96.2467*	*-56.5822*	*-0.0291*	*-18.27*	*1.822*	*141.06*
9	D9	i	-113.5384	-56.9167	-56.5822	-0.0394	-24.75	1.683	149.43
10	D10	a	-270.8136	-135.5718	-135.2081	-0.0336	-21.10	1.722	155.60
11	B1	i	-113.5275	-56.9180	-56.5821	-0.0275	-17.23	1.843	130.09
12	B2	e	-192.1671	-96.2466	-95.8932	-0.0273	-17.15	1.834	134.38
13	Sp	j	-349.4711	-174.9038	-174.5412	-0.0261	-16.38	1.882	132.67
		i	*-113.5272*	*-56.9173*	*-56.5816*	*-0.0283*	*-17.75*		
14	Hp	i	-113.5104	-56.9177	-56.5814	-0.0113	-7.10	1.960	110.70
15	P1	i chair	-113.4979	-56.9195	-56.5817	0.0033	2.07	2.339	85.85
16	P2	f boat	-152.8262	-96.2478	-56.5818	0.0034	2.16	2.288	90.24
17	P3	e boat	-192.1414	-96.2479	-95.8932	-0.0003	-0.18	2.319	90.39
11A	O1	i	-113.5258	-56.9159	-56.5810	-0.0289	-18.14	1.737	134.17
12A	O2	e	-192.1660	-96.2449	-95.8923	-0.0288	-18.07	1.732	138.55

[a] Numeric identifier of compound in Table S6 of isodesmic reactions

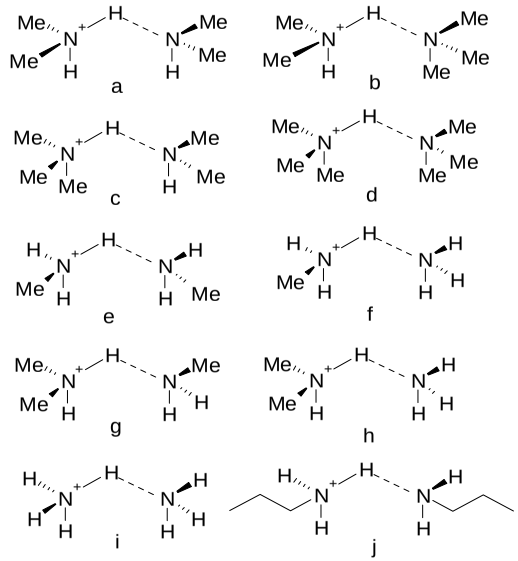
[b] Structures of compouds are given in Schemes 1, 2 and S1.

[c] Hydrogen bond complex in Scheme S2

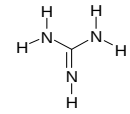
[d] E(HB) = E(Complex) - E(HD) -E(HA), 1 AU = 627.5 kcal mol^{-1}

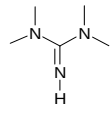
Rows in italic contain reference calculations

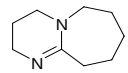
Scheme S2. Hydrogen Bond Complex.

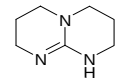


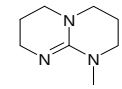
Scheme S3. Structures of the "Other" Bases in Table 1.[a]

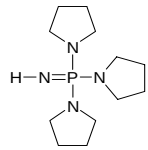

Guanidine

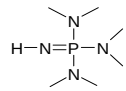

TMG

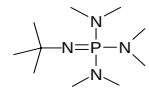

DBU

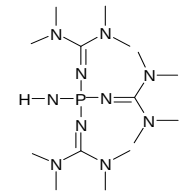

TBD

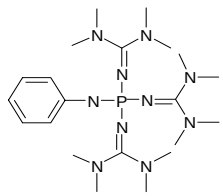

MTBD

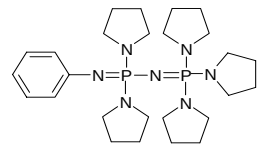

HP_1(pyrr)

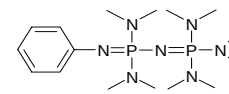

HP_1(dma)

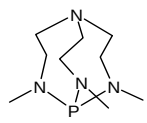

*t*BuP_1(dma)


HP_1(tmg)


PhP_1(tmg)


PhP_2(pyrr)


PhP_2(dma)


Verkade's Base

[a] Some srtuctures not shown here are in SI Scheme S1: **R7** as PhTMG, **R19** as *t* BuP_1(pyrr), **R3** as PhP_1(pyrr), **R6** as PhP_1(dma) and **R20** as EtP_2(dma).

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Main scientific publications

1. Acid-Base Equilibria in Nonpolar Media. 3. Expanding the Spectrophotometric Acidity Scale in Heptane. Rõõm, E.-I.; Kaljurand, I.; Leito, I.; Rodima, T.; Koppel, I. A.; Vlasov, V. M. *J. Org. Chem.* **2003**, *68*, 7795–7799.

2. Self-consistent Acidity and Basicity Scales in Nonaqueous Solvents. Leito I.; Kaljurand I.; Rodima T.; Kütt A.; Pihl A.; Rõõm E.-I.; Sooväli L.; Mäemets V.; Pihl V.; Koppel I. A. *Proceedings of the Estonian Academy of Sciences Chemistry.* **2005**, *54*, 94–115.
3. Uncertainty Sources in UV-Vis Spectrophotometric Measurement. Sooväli, L.; Rõõm, E.-I.; Kütt, A.; Kaljurand, I.; Leito, I. *Accreditation and Quality Assurance* **2006,** *11* (5), 246–255.
4. Experimental Gas-Phase Basicity Scale of Superbasic Phosphazenes. Kaljurand, I.; Koppel, I. A.; Kütt, A.; Rõõm, E.-I.; Rodima, T.; Koppel, I.; Mishima, M.; Leito, I. *J. Phys. Chem. A* **2007**, *111*, 1245–1250.
5. Brønsted Acidity of Neutral and Cationic Acids in Nonaqueous Solvents: Recent developments. Leito, I.; Kütt, A.; Kaljurand, I.; Rõõm, E.-I.; Rodima, T.; Koppel, I. A. Abstracts of Papers, 233rd ACS National Meeting, Chicago, IL, United States, March 25–29, **2007**, *INOR-1036*. American Chemical Society: Washington, DC.
6. Brønsted Basicities of Diamines in the Gas Phase, Acetonitrile and Tetrahydrofuran. Rõõm, E.-I.; Kütt, A.; Kaljurand, I.; Koppel, I.; Leito, I.; Koppel, I. A.; Mishima, M.; Goto, K.; Miyahara, Y. *Chem. Eur. J.* **2007**, *accepted*.
7. Anions $N[C(CN)_2]_3^-$ and $P[C(CN)_2]_3^-$and the Superacidic Properties of their Conjugate Acids. Leito, I.; Kütt, A.; Rõõm E.-I.; Koppel I. A. *J. Mol. Stru. THEOCHEM*, **2007**, *accepted*.

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Tähtsamad teaduspublikatsioonid

1. Acid-Base Equilibria in Nonpolar Media. 3. Expanding the Spectrophotometric Acidity Scale in Heptane. Rõõm, E.-I.; Kaljurand, I.; Leito, I.; Rodima, T.; Koppel, I. A.; Vlasov, V. M. *J. Org. Chem.* **2003**, *68*, 7795–7799.
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3. Uncertainty Sources in UV-Vis Spectrophotometric Measurement. Sooväli, L.; Rõõm, E.-I.; Kütt, A.; Kaljurand, I.; Leito, I. *Accreditation and Quality Assurance* **2006,** *11* (5), 246–255.
4. Experimental Gas-Phase Basicity Scale of Superbasic Phosphazenes. Kaljurand, I.; Koppel, I. A.; Kütt, A.; Rõõm, E.-I.; Rodima, T.; Koppel, I.; Mishima, M.; Leito, I. *J. Phys. Chem. A* **2007**, *111*, 1245–1250.
5. Brønsted Acidity of Neutral and Cationic Acids in Nonaqueous Solvents: Recent developments. Leito, I.; Kütt, A.; Kaljurand, I.; Rõõm, E.-I.; Rodima, T.; Koppel, I. A. Abstracts of Papers, 233rd ACS National Meeting, Chicago, IL, United States, March 25–29, **2007**, *INOR-1036*. American Chemical Society: Washington, DC.
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