Spanning and Expanding the Basicity Scale with Simple Ammonia Derivatives[†]

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The currently known intrinsic basicity ($\Delta G°$) range spans about 154 kcal/mol, from the basicity of the oxygen molecule (94.7 kcal/mol) to that of 7-isopropyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (248.4 kcal/mol). In this paper, we show that the basicities of two commercially available derivatives of ammonia, viz. F_3N and Li_3N, differ by 182 kcal/mol, which is greater than the above-mentioned range. We also show that the basicity range from F_3N to Li_3N can be spanned with simple ammonia derivatives containing single-atom substituents of electronegativity higher or lower than that of nitrogen and that basicities even higher than that of Li_3N (a superbase) are indeed possible. The large basicity differences exhibited by these compounds are analyzed in the light of the energies of their charged and neutral forms. It should be noted that the most basic compounds reported fill the current gap between the intrinsic acidity and basicity scales, which allows such basic substances to be inserted in the known acidity range for neutral compounds in order to generate the corresponding conjugate charged forms by reacting in the gas phase an appropriate acid with a neutral base.

Introduction

The existing basicity scale is very broad; in fact, it encompasses $\Delta G°$ values from 94.7 kcal/mol for the oxygen molecule to 248.4 kcal/mol for 7-isopropyl-1,5,7-triazabicyclo[4.4.0]decene.[1] This has largely been the result of the research efforts of the groups headed by Bowers (Santa Barbara), Brauman (Stanford), Kebarle (Edmonton), Mautner (Gaithersburg), and Taft (Irvine), among others, in the past few decades. However, the search for superbases with $\Delta G°$ values above 250 kcal/mol and superacids with ΔG_{acid} values below 285 kcal/mol appears to be stalled—the strongest acid identified to date is $(C_4F_9SO_2)_2NH$, with $\Delta G_{\mathrm{acid}} = 284.1$ kcal/mol.[2] Therefore, any attempts at breaking this deadlock by finding more powerful acids or bases is in principle welcome.

Recently, our group showed that ab initio calculations at the DFT[B3LYP(6-311+G(3df,3pd))] level[3] allow the determination of ΔG acidity or basicity values for neutral molecules that are quite consistent (SD = 1.35 kcal/mol) with their experimental counterparts by using the expression

$$\Delta G°_{\mathrm{exp}} = [1.0028(\pm 0.0028)]\Delta G°_{\mathrm{theor}} + 0.52(\pm 0.78)$$

This equation includes $\Delta G°_{\mathrm{exp}}$ and $\Delta G°_{\mathrm{theor}}$, which reflect both the basicity of rather different neutral molecules such as N_2, HF, HCl, C_2H_2, H_2O, CH_3OH, CH_3CN, NH_3, and imidazole and the acidity of widely different neutral acids such as HPO_3, H_2SO_4, HCl, HBr, NaH, pyrrole, HF, CH_3OH, H_2O, NH_3, and CH_4.

Our results allow us not only to confirm the consistency between the intrinsic acidity and basicity scales but also to show that calculations at this level are powerful tools for identifying new potential superacids and superbases such as those required in this work to fill the gap between the two scales.

On the basis of electronegativity criteria, we chose single-atom substituents (−F, −Li, and −Na) to replace the hydrogen atoms in ammonia in order to demonstrate that a straightforward procedure allows one to establish a series of compounds ranging from a scarcely basic compound such as ammonia to more basic substances, including several superbases, with a view to filling the present gap with the acidity scale or even reaching beyond that point. Finding a substance of basicity greater than 285 kcal/mol would allow a neutral acid and base to spontaneously produce their corresponding charged acid and basic forms according to

$$B_{(g)} + HA_{(g)} \rightleftarrows BH^+_{(g)} + A^-_{(g)}$$

We shall also try to explain the origin of the broad differences in basicity among these compounds by examining their protonated and neutral forms.

Method

Application of methods based on the density functional theory (DTF) to the study of molecular properties has recently experienced a spectacular increase. All the DFT molecular computations reported here were performed with the Gaussian 94[4] series of programs using the 6-311+G(3df,3pd)[5] basis set.

For the DFT computation, we used a hybrid functional as implemented in Gaussian 94. The hybrid functional corresponds to Becke's three-parameter exchange functional

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[†] Dedicated to the memory of Robert W. Taft.

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(B3LYP).[6a] When the Gaussian 94 formalism is followed, this functional can be written in the form

$$0.80[E(\mathrm{S})_\mathrm{x}] + 0.20[E(\mathrm{HF})_\mathrm{x}] + 0.72[E(\mathrm{B88})_\mathrm{x}] + 0.19[E(\mathrm{Local})_\mathrm{c}] + 0.81[E(\mathrm{LYP})_\mathrm{c}] \quad (1)$$

where $E(\mathrm{S})_x$ is the Slater exchange,[6b,c] $E(\mathrm{HF})_x$ is the Hartree−Fock exchange, $E(\mathrm{B88})_x$ represents Becke's 1988 nonlocal exchange functional corrections,[6d] $E(\mathrm{Local})_\mathrm{c}$ corresponds to the Vosko, Wilk, and Nusair local correlation functional,[6e] and $E(\mathrm{LYP})_\mathrm{c}$ corresponds to the correlation functional of Lee, Yang, and Parr[6f,g] (including both local and nonlocal terms). We later demonstrated that this computational procedure can predict the acid−base molecular properties of a wide variety of compounds within experimental error.[3]

The Gibbs energy of protonation, $\Delta G°$, of a molecule B is defined as an increment of the free energy corresponding to the process (2).

$$\mathrm{B}_{(g)} + \mathrm{H^+}_{(g)} \rightarrow \mathrm{BH^+}_{(g)} \quad (2)$$

The expression for evaluating $\Delta G°(\mathrm{B})$ is given by eq 3, where

$$\Delta G°(\mathrm{B}) = -\Delta G°(2) = -\Delta H°(2) + T[\Delta S°(2)] \quad (3)$$

$\Delta H°(2)$ includes the differences between the reactants (B) and products ($\mathrm{BH^+}$) in the electron energies at 0 K, the zero-point energies, and the thermal energy corrections, which contain the effects of molecular translation, vibration, and rotation estimated at 298.15 K and 1 atm. $\Delta S°(2)$ includes the entropy difference between the base (B) and its conjugate acid ($\mathrm{BH^+}$), as well as an entropy term due to the proton that is calculated using the Sakur−Tetrode equation,[7] and one arising from potential symmetry changes in process 2 that can be calculated from

$$T[\Delta S^\circ_{\mathrm{sym}}] = RT\,\ln(\sigma_{\mathrm{BH}}/\sigma_{\mathrm{B}})$$

The corresponding $3N - 6$ vibrational frequencies for each molecular structure studied can be supplied by the author upon request.

Results and Discussion

Geometries and Salient Quantities for the Compounds Studied. Halogenated Ammonia. Like ammonia, its halogenated derivatives possess a pyramidal structure typical of tetragonal hybridization at its nitrogen atom. We found the length of the N−F bond in fluorine-substituted compounds to considerably decrease with an increase in the number of F atoms present in the compound; in fact, it decreases from 1.427 Å for $\mathrm{FH_2N}$ to 1.397 Å ($r_\mathrm{e}^{\mathrm{exp}} = 1.400 \pm 0.002$ Å[8]) for $\mathrm{F_2HN}$ to 1.375 Å ($r_\mathrm{e}^{\mathrm{exp}} = 1.371 \pm 0.002$ Å[9]) for $\mathrm{F_3N}$. On the other hand, the length of the N−H bond hardly changes among these compounds. Table 1 shows their more relevant structural parameters. As can be seen, the structure of $\mathrm{Cl_3N}$ is also pyramidal. Table 2 gives the rotational constants for these structures; note the high consistency between theoretical and experimental data for ammonia, nitrogen difluoride, and nitrogen trifluoride.

Table 1. Theoretical and Experimental (in Parentheses) Bond Distances (Å) and Bond Angles (deg) for the Molecular Structures Studied

compd	r_{NH}	r_{NX}	θ_{HNH}	θ_{HNX}	θ_{XNX}
$\mathrm{NH_3}$	1.013		107.2		
	(1.0136)[a]		(107.1)[a]		
$\mathrm{NH_2F}$	1.020	1.427	105.5	101.6	
$\mathrm{NHF_2}$	1.026	1.397		100.1	103.6
	(1.026)[b]	(1.400)[b]		(99.8)[b]	(102.9)[b]
$\mathrm{NF_3}$		1.375			102.0
		(1.371)[c]			(102.1)[c]
$\mathrm{NCl_3}$		1.771			108.5
$\mathrm{NH_2Li}$	1.015	1.731	104.3	127.9	
$\mathrm{NHLi_2}$	1.023	1.736		113.2	133.7
$\mathrm{NLi_3}$		1.716			120.0
$\mathrm{NH_2Na}$	1.016	2.097	104.4	124.2	
$\mathrm{NHNa_2}$	1.031	2.130		104.5	124.6
$\mathrm{NNaLi_2}$		2.105[d]			116.9[e]
		1.718			126.0[f]
$\mathrm{NH_4^+}$	1.024		109.5		
$\mathrm{NFH_3^+}$	1.031	1.363	111.2	107.7	
$\mathrm{NF_2H_2^+}$	1.038	1.338	115.1	108.1	109.4
$\mathrm{NF_3H^+}$	1.047	1.322		110.1	108.8
$\mathrm{NCl_3H^+}$	1.026	1.753		106.3	112.5
$\mathrm{NLiH_3^+}$	1.019	1.962	105.1	113.6	
$\mathrm{NLi_2H_2^+}$	1.022	1.872	102.5	105.2	130.6
$\mathrm{NLi_3H^+}$	1.032	1.811		100.3	116.9
$\mathrm{NNaH_3^+}$	1.018	2.342	105.2	113.4	
$\mathrm{NNa_2H_2^+}$	1.022	2.232	102.1	103.6	136.0
$\mathrm{NNaLi_2H^+}$	1.031	2.208[d]		95.4[g]	116.3[e]
		1.799		102.6	118.1

[a] Reference 10. [b] Reference 8. [c] Reference 9. [d] r_{NNa}. [e] θ_{NaNLi}. [f] θ_{LiNLi}. [g] θ_{HNLi}.

Table 2. Theoretical and Experimental (in Parentheses) Rotational Constants (in GHz) and Dipole Moments μ (D) of the Neutral Molecular Structures Studied

compd	A	B	C	μ
$\mathrm{NH_3}$	299.561	299.561	188.612	1.51 (1.472)[d]
	(298.144)[a]	(298.144)[a]	(189.139)[a]	
$\mathrm{NFH_2}$	265.836	26.496	25.483	2.30
$\mathrm{NF_2H}$	53.509	10.832	9.290	1.94 (1.92 ± 0.02)[b]
	(53.017)[b]	(10.895)[b]	(9.307)[b]	
$\mathrm{NF_3}$	10.629	10.629	5.820	0.22 (0.234)[e]
	(10.681)[c]	(10.681)[c]	(5.844)[c]	
$\mathrm{NCl_3}$	3.399	3.399	1.757	0.37 (0.39 ± 0.01)[f]
$\mathrm{NLiH_2}$	390.602	30.354	28.165	4.79
$\mathrm{NLi_2H}$	99.406	14.130	12.372	3.77
$\mathrm{NLi_3}$	16.306	16.306	8.153	0.00
$\mathrm{NNaH_2}$	361.172	11.206	10.916	6.42
$\mathrm{NNa_2H}$	38.937	3.079	2.874	4.06
$\mathrm{NNaLi_2}$	15.360	6.096	4.364	0.61

[a] Reference 11. [b] Reference 8. [c] Reference 9. [d] Reference 12. [e] Reference 13. [f] Reference 14.

As expected, the dipole moment decreased dramatically from ammonia ($\mu_{\mathrm{th}} = 1.51$, $\mu_{\mathrm{exp}}(\mathrm{gas}) = 1.472^{12}$) to trihalogenated derivatives such as $\mathrm{Cl_3N}$ ($\mu_{\mathrm{th}} = 0.37$, μ_{exp}(gas)

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= 0.39 ± 0.01[14]) and F_3N ($\mu_{th} = 0.22$, $\mu_{exp}(gas) = 0.234 \pm 0.02$[13]). Accordingly, the dipole moment for fluoroammonia derivatives decreased from FH_2N ($\mu_{th} = 2.30$) to F_2HN ($\mu_{th} = 1.94$, $\mu_{exp}(gas) = 1.92$[8]) to F_3N ($\mu_{th} = 0.22$, $\mu_{exp}(gas) = 0.234$[13]). Table 2 gives the dipole moment for the studied structures.

Alkali-Metal-Substituted Ammonia. Surprisingly, the three compounds of formula $Li_nH_{3-n}N$ studied exhibit a structural peculiarity: they are planar, so its nitrogen atom possesses trigonal hybridization. As can be seen from Table 1, N−Li distances in these compounds follow no clear-cut trend in relation to the number of lithium atoms; in fact, the N−Li bond distance is 1.731 Å in LiH_2N, 1.736 Å in Li_2HN, and 1.716 Å in Li_3N.

In summary, the lithium derivatives of ammonia adopt a planar geometry if other substituents of the compound under consideration ($NNaLi_2$, NLi_3, $NHLi_2$, and NH_2Li) acquire a positive partial charge ($-H^{\delta+}$, $-Li^{\delta+}$, and $-Na^{\delta+}$). On the other hand, the compounds NF_2Li, NCl_2Li, and NHFLi become pyramidal, if some substituents (e.g., $-F^{\delta-}$ and $-Cl^{\delta-}$) become negatively charged. A feasible explanation could be that the positive charge, which is localized in the lithium substituent, is stabilized due to electrostatic interactions: (a) merely with the electron pair of the nitrogen, thereby adopting a planar geometry, or (b) also with other negatively charged substituents of the compound by achieving a pyramidal geometry.

In contrast, the sodium counterparts (viz. NaH_2N and Na_2HN) exhibit a pyramidal structure; $-Na_3N$ is unstable because its optimized structure has a negative vibration. It should be noted that Li_2NaN is planar. The structures of these compounds are shown in Table 1. Table 2 gives the rotational constants and dipole moments for all the alkali-metal-substituted compounds studied.

On the basis of symmetry considerations, Li_3N is nonpolar ($\mu_{th} = 0.0$) and Li_2NaN is only slightly polar ($\mu_{th} = 0.61$). However, by virtue of the ionic character of N−Li and N−Na bonds, the mono- and disubstituted derivatives are markedly polar—particularly the mono derivatives, with $\mu_{th} = 4.79$ for LiH_2N versus 3.77 for Li_2HN, and $\mu_{th} = 6.42$ for NaH_2N versus 4.06 for Na_2HN.

Protonated Forms. The most relevant structural facts for the protonated forms are as follows. (a) All exhibit a pyramidal structure—even those produced from the compounds of formula $Li_nH_{3-n}N$, which are planar. (b) N−F distances are shorter relative to the neutral forms but continue to decrease with an increasing number of fluorine atoms (1.365, 1.338, and 1.322 Å for FH_2N, F_2HN, and F_3N, respectively). (c) In contrast, the distances between the nitrogen and the alkali-metal atoms are significantly longer than those in the neutral forms and thus decrease with an increasing number of alkali-metal atoms in the molecular structure. Thus, the N−Li bond distance is 1.73 Å in LiH_2N and 1.96 in LiH_3N^+, and the N−Na distance is 2.097 in NaH_2N and 2.342 Å in NaH_3N^+. The more relevant structural data for these protonated forms are reported in Table 1.

Basicity of the Compounds Studied. Table 3 gives the Gibbs energies for the neutral and protonated forms of the compounds examined, as well as their calculated intrinsic basicities, which are consistent with those of their experimental counterparts. Thus, Hunter and Lias[1b] recently reported the basicity of ammonia to be 195.8 kcal/mol, which is very similar to the calculated value in the absence of symmetry correction (194.7 kcal/mol). Worthy of special comment is the basicity of F_3N; Lias et al.[1a] reported a value of 136 kcal/mol on the basis of the bracketing experiment conducted by Doiron and McMahon,[15] which placed the basicity of this compound between those of CO and CH_3F. On the basis of subsequent experiments of McMahon and Kebarle,[16] Hunter and Lias[1b] reevaluated this quantity and found it to be 128.6 kcal/mol, which is more consistent with the result obtained in this work (123.4 kcal/mol).

Table 3. Free Energies (in au) of the Neutral ($G°(B)$) and Protonated Bases ($G°(BH^+)$), Free Energy Increments of Protonation ($\Delta G°(2)$, in kcal mol^{-1}) Obtained from Eq 2, and Energies of Stabilization with Respect to the Atomic Constituents[a] of These Forms for Neutral (ΔG_n, in kcal mol^{-1}) and Protonated (ΔG_p, in kcal mol^{-1}) Species Relative to Ammonia (NH_3) and Ammonium Ion (NH_4^+), Respectively

compd	$G°(B)$	$G°(BH^+)$	$-\Delta G°(2)$	ΔG_n	ΔG_p
NH_3	−56.571 35	−56.893 99	193.8	0.0	0.0
NFH_2	−155.776 69	−156.063 13	171.7	+36.6	+59.3
NF_2H	−255.000 09	−255.249 50	148.3	+61.9	+107.8
NF_3	−354.234 31	−354.443 44	123.4	+80.2	+149.6
NCl_3	−1 435.359 06	−1 435.629 61	162.0	+112.4	+145.1
$NLiH_2$	−63.509 48	−63.921 01	249.8	+25.4	−30.4
NLi_2H	−70.426 03	−70.897 91	287.9	+64.2	−29.4
NLi_3	−77.347 04	−77.846 21	305.4	+100.2	−10.4
$NNaH_2$	−218.270 33	−218.707 22	265.6	+56.6	−15.2
NNa_2H	−379.945 97	−380.449 70	307.9	+127.7	+14.0
$NNaLi_2$	−232.106 16	−232.616 28	312.3	+132.6	+14.9

[a] The corresponding free energy values (in au) of the atoms used are as follows: $G°(N) = -54.615\ 76$, $G°(Li) = -7.491\ 33$, $G°(F) = -99.776\ 49$, $G°(H) = -0.512\ 81$, $G°(Na) = -162.301\ 86$, and $G°(Cl) = -460.168\ 41$.

We should note that fluorinated ammonias allow the basicity to be sequentially reduced (by about 23 kcal/mol per fluorine atom) to the bottom of the basicity scale (F_3N has an estimated basicity of 123 kcal/mol). This behavior clearly reflects that the fluorine atom is more electronegative than the nitrogen; also, by virtue of the higher electronegativity of fluorine relative to chlorine, Cl_3N is considerably more basic ($\Delta G° = 162.0$ kcal/mol) than F_3N ($\Delta G° = 123.7$ kcal/mol).

Conversely, replacing hydrogen atoms in ammonia with much less electronegative atoms such as Li and Na substantially increases the basicity of the resulting compounds relative to ammonia. As can be seen from Figure 1, this effect allows one not only to fill the gap between the basicity and acidity scales with commercially available compounds such as lithium amide and sodium amide but also to reach the typical range of the acidity scale with compounds such as Li_2HN, Li_3N, Na_2HN, and Li_2NaN, which clearly cross the threshold of the acidity scale, established at $\Delta G°_{acid} = 284$ kcal/mol.

The basicity data shown in Table 3 for alkali-metal−ammonia derivatives allow us to conclude that replacing a hydrogen atom in ammonia with a lithium or sodium atom considerably increases the basicity of the compound (by about 55.9 kcal/mol for Li and 71.1 kcal for Na). A further, though less marked, increase is produced by a

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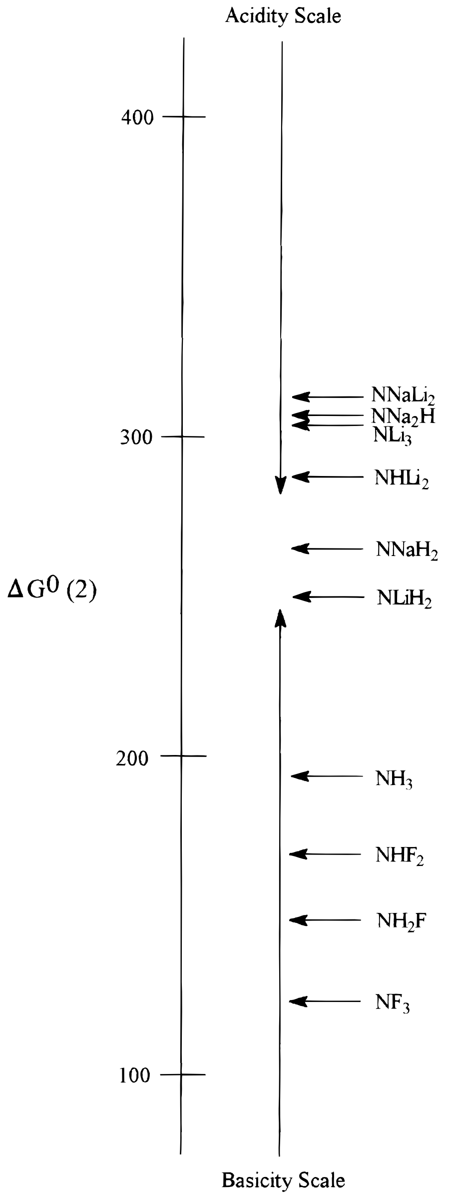

Figure 1.

second substitution (38.1 and 42.3 kcal/mol for Li and Na, respectively). Introducing a third lithium atom increases the basicity by a further 17.1 kcal/mol and makes Li_3N a true superbase, with $\Delta G° = 305.4$ kcal/mol. Our calculations suggest that Na_3N cannot be stable, as it exhibits a negative vibrational frequency; therefore, its optimized structure cannot represent a true minimum in the potential energy surface. However, the increased basicity resulting from substitution of the protons in ammonia by lithium or sodium atoms allow one to estimate the basicity for this molecule—were it stable, it would be a superbase with $\Delta G° \simeq 324$ kcal/mol.

While the above-described changes in the basicity of ammonia with substitutions by fluorine, lithium, or sodium atoms must originate from electronegativity differences, the magnitudes of the changes suggest the potential occurrence of destabilizing effects such as electrostatic repulsions between substituents with net charges ($-F^{\delta-}$, $-Li^{\delta+}$, and $-Na^{\delta+}$), which may account, among others, for such special structural features as the fact that the neutral forms of the Li-substituted derivatives possess a planar geometry.

Table 4. Stabilization of the Neutral and Protonated Molecular Forms Studied, Given in Increasing Sequence Relative to Ammonia and Ammonium Ion, Respectively

neutral form	$\Delta G°_n$ (kcal mol^{-1})	protonated form	$\Delta G°_p$ (kcal mol^{-1})
$NNaLi_2$	+132.6	NF_3H^+	+149.6
NNa_2H	+127.7	NCl_3H^+	+145.1
NCl_3	+112.4	$NF_2H_2^+$	+107.8
NLi_3	+100.2	NFH_3^+	+59.3
NF_3	+80.2	$NNaLi_2H^+$	+14.9
NLi_2H	+64.2	$NNa_2H_2^+$	+14.0
NF_2H	+61.9	NH_4^+	0.0
$NNaH_2$	+56.6	NLi_3H^+	−10.4
NFH_2	+36.6	$NNaH_3^+$	−15.2
$NLiH_2$	+25.4	$NLi_2H_2^+$	−29.4
NH_3	0.0	$NLiH_3^+$	−30.4

Because the basicity of a compound results from energy differences between its protonated and neutral forms, it seems logical to analyze the effect of substitutions on the energies of both the neutral and the protonated forms. To this end, it is of interest to determine the stabilization energy of these forms relative to the individual atoms (evaluated by the same method), obviously with reference to ammonia (ΔG_n) for the neutral forms and to ammonium ion (ΔG_p) for the protonated forms, using the expressions

$$\Delta G_n = G^\circ_{mol(n)} - G_{\Sigma atoms[mol(n)]} - G^\circ_{NH_3} + G_{\Sigma atoms(NH_3)]}$$

$$\Delta G_p = G^\circ_{mol(p)} - G_{\Sigma atoms[mol(p)]} - G^\circ_{NH_4^+} + G_{\Sigma atoms(NH_4^+)]}$$

Table 3 shows the stabilization and destabilization energies for the neutral (ΔG_n) and protonated forms (ΔG_p) of substituted ammonia relative to ammonia and ammonium ion, respectively; obviously, ammonia and ammonium ion are assumed to have zero ΔG_n and ΔG_p values, respectively. Table 4 shows both neutral and protonated forms in ascending order of stability. Any of the ammonia substitutions studied leads to a situation more unstable than that of unsubstituted ammonia; also, the ensuing instability increases with an increasing number of substituents and electronegativity. Thus, except for Na_2HN, the most unstable derivatives are the trisubstituted derivatives, followed by the disubstituted ones and, finally, those with a single substituent; i.e., any substitution destabilizes the neutral form, so that it tends to increase the basicity relative to unsubstituted ammonia. On the other hand, protonated forms only follow this trend in those derivatives containing substituents of electronegativity higher than that of nitrogen (i.e. −F and −Cl); it should be noted that the protonated forms of the lithium derivatives and the monosodium derivative are more stable than ammonium ion. Since $\Delta G_p - \Delta G_n$ represents the basicity difference between any of these compounds and ammonia, we can analyze the effect of substitution on its basicity.

Fluoride atoms decrease the basicity of ammonia because the protonated forms of the resulting derivatives are more unstable than their neutral counterparts (see Table 3); interestingly, the two are proportional ($\Delta G_p = 1.7[\Delta G_n]$) and each fluorine atom introduced decreases the basicity of ammonia by about 23 kcal/mol. Lithium substitution produces a different effect; thus, the first Li atom increases the basicity of ammonia to a similar extent through destabilization of the neutral form and stabilization of the protonated one. As can be seen from Table 3, the increased effect of the number of lithium atoms arises from the destabilization they introduce in the corresponding neutral forms. On the basis of the data of Table 3, this effect is also exerted by sodium, to an even greater extent.

These effects of alkali-metal or halogen substitutions are somewhat novel, since the usual result in this type of analysis is that basicity changes within a compound family are governed by stability changes in the protonated forms of the compounds because those in the neutral forms are usually small by contrast.[17,18]

As can be seen from Table 3 and Figure 1, we have found four compounds that clearly cross the threshold of the acidity region; therefore, by confronting the substances with others of acidity between 284 and 314 kcal/mol, one can establish equilibria between a base and its conjugate acid, leading to the charged conjugate forms resulting from proton transfer in the gas phase. By way of example, let us consider the behavior of the most basic substances examined in this work (viz. $NaLi_2N$, Na_2HN, and Li_3N, with $\Delta G°$ values of 312.3, 307.9, and 305.4 kcal/mol, respectively) toward strong mineral acids (viz. HI, HPO_3, H_2SO_4, and $HClO_4$, with ΔG_{acid} values of 309.2, 303.3, 302.3, and 291.9 kcal/mol, respectively). $NaLi_2N$ will deprotonate HI to a high degree and the other, stronger acids (HPO_3, H_2SO_4, $HClO_4$) completely; on the other hand, Na_2HN and Li_3N will deprotonate HPO_3 to an appreciable extent and the remaining, stronger acids (H_2SO_4 and $HClO_4$) according to the equilibria

$$NaLi_2N + HI \rightleftarrows NaLi_2NH^+ + I^- \qquad \Delta G° = -3.1 \text{ kcal/mol}$$

$$Na_2HN + HPO_3 \rightleftarrows Na_2NH^+ + PO_3^- \qquad \Delta G° = -4.6 \text{ kcal/mol}$$

$$Li_3N + HPO_3 \rightleftarrows Li_3NH^+ + PO_3^- \qquad \Delta G° = -2.1 \text{ kcal/mol}$$

$$Li_3N + H_2SO_4 \rightleftarrows Li_3NH^+ + HSO_4^- \qquad \Delta G° = -3.2 \text{ kcal/mol}$$

$$Li_3N + HClO_4 \rightleftarrows Li_3NH^+ + ClO_4^- \qquad \Delta G° = -13.5 \text{ kcal/mol}$$

Conclusions

As shown in this work, simple ammonia derivatives obtained by replacing its hydrogen atoms with single-atom substituents of electronegativity greater or lesser than that of nitrogen allows one not only to span the whole basicity range from F_3N to Li_3N but also to reach beyond the latter into the current acidity region for neutral substances with a superacid character. In contrast to the results for other families of basic compounds, cumulative instability in the neutral forms of the substances studied here is the origin of the strong basicity differences among them—so strong, in fact, that some derivatives behave as true superbases.

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