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Quest for the Origin of Basicity: Initial vs Final State Effect in Neutral Nitrogen Bases

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The problem of the origin of the intrinsic basicity of neutral nitrogen bases, as reflected in their gas phase proton affinities, is addressed and a simple solution is found. It is rooted in an intuitively appealing picture involving ionization of the base in question by pruning an electron, subsequent creation of the hydrogen atom with the incoming proton, and the formation of the homolytic chemical bond between a radical cation and the hydrogen. The role of the initial state (base) is mirrored by the ionization potential of the pruned electron given by Koopmans' approximation, whereas the contribution of the final state (conjugate acid) encompasses the electron affinity of the proton, the relaxation energy of the produced radical cation, and finally the homolytic bond association energy of the newly formed N−H bond. This dissection of the protonation process into three sequential steps has a high cognitive value, enabling classification of bases into three categories at the same time. The first is given by compounds such as ammonia and its alkylated derivatives, the basicity of which is dictated by the initial state effect. The second grouping is formed by those molecules in which the final-state effects decisively influence their basicity values such as, e.g., in methyleneimine and its amino derivatives, whereas the last category encompasses systems exhibiting basicities governed by an interplay between the initial and final-state properties. Phosphazenes belong to the latter set of compounds. Finally, the solvent effect in acetonitrile is considered and briefly discussed within the context of the isodensity polarized continuum model (IPCM). It is shown that a correct hierarchy of basicity in the $NH_{3-n}(Me)_n$ series requires explicit account of the solvent effect. Although the present analysis is quite general, it should be particularly useful in discussing trends of changes in basicities of intimately related molecules.

1. Introduction

There is a tremendous interest in the basicity and the accompanying proton affinity (PA) of neutral organic molecules, with a particular emphasis on the superbasic systems.[1−4] This is not unexpected in view of the important role of the proton transfer reaction in organic chemistry and biochemistry.[5,6] Modern computational chemistry can aid the experimental studies in two complementary ways: (1) to predict new molecular systems exhibiting desired properties (i.e., basicities) and (2) to interpret the data using simple and intuitively appealing chemical concepts, thus contributing to a deeper and better understanding of the protonation process. These two aspects are closely related because rationalization of the trends of changes in the proton affinity by recognizing the underlying fundamental principles enables an easier architecture and design of new superbases, for example.

We address here the question of the origin of the intrinsic basicity of neutral bases. The simplest interpretation of the proton affinity of nitrogen atom in molecular environments is given by a relation to the hybridization s-character of its lone pair. The idea behind this picture is that a higher s-character implies a more negative energy of the lone pair electrons. Consequently, a higher energetic price has to be paid when a new $[N{-}H]^+$ bond is formed, leading ultimately to smaller PA values.[7,8] Essentially the same idea yields a correlation between the PAs and the ionization potentials (IPs).[9,10] Although these two simple and appealing models are of some value, they describe only a part of the protonation process. Hence, their applications are limited, being confined to small families of very closely related compounds. The same conclusion applies to the relationship between the electron densities of atoms to be protonated and the proton affinities. A more detailed discussion of the relation between the PAs and ESCA shifts is given at the end of the paper.

It would be useful to have at one's disposal a more general description of the protonation event, which could offer a more comprehensive and deeper understanding of the susceptibility of organic bases toward the proton. This is of importance because (over)simplified models could be misleading and yet they are used in the literature. In particular, we shall focus on nitrogen compounds, since they provide the most powerful neutral bases in organic chemistry. It will appear that the initial state (base) and final state (conjugate acid) effects can be delineated in a straightforward and transparent way.

At the end of the paper we shall dwell on the problem of the solvent effect in moderately polar aprotic solvents exemplified by acetonitrile and discuss its relation to the proton affinities in the gas phase.

2. Theoretical Basis

We shall analyze the intrinsic or gas-phase proton affinity by using the following equation:

$$B + H^+ \rightarrow (B_\alpha H)^+ + (PA)_\alpha \tag{1}$$

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where B denotes a base in question and α stands for the site of the proton attack. In our case the latter will be the lone pair of a particular nitrogen atom. The second important equation describes ionization of the base under scrutiny:

$$\mathrm{B} - \mathrm{e}^- \rightarrow \mathrm{B}_\alpha^{+\bullet} - (\mathrm{IP})_1^{\mathrm{ad}} \qquad (2)$$

Here $(\mathrm{IP})_1^{\mathrm{ad}}$ signifies the first adiabatic ionization potential describing ejection of the least bound electron and simultaneous formation of the corresponding radical cation ($\mathrm{B}_\alpha^{+\bullet}$). Finally, if the radical cation and hydrogen atom unite forming the conjugate acid, then the following relation holds:

$$\mathrm{B}_\alpha^{+\bullet} + \mathrm{H}^\bullet \rightarrow (\mathrm{B}_\alpha\mathrm{H})^+ + (\mathrm{BAE})_\alpha^+ \qquad (3)$$

where $(\mathrm{BAE})_\alpha^+$ gives the bond association energy of the homolytic bond formation between the radical cation $\mathrm{B}_\alpha^{+\bullet}$ and the hydrogen atom. It is easy to show, by combining eqs. 1−3, that the proton affinity is determined by eq 4:

$$(\mathrm{PA})_\alpha = (\mathrm{BAE})_\alpha^+ - (\mathrm{IP})_1^{\mathrm{ad}} + \mathrm{EA}(\mathrm{H}^+) \qquad (4)$$

Here $\mathrm{EA}(\mathrm{H}^+)$ is the electron affinity of the proton being 13.6 eV. Equation 4 is important because of two reasons: (a) it is rigorous and (b) has a very high interpretive value. The underlying physical picture is very simple. The protonation can be decomposed in three steps: (1) ionization of the base B by ejection of an electron, (2) capture of the expelled electron by the proton with concomitant formation of a neutral hydrogen atom, and (3) homolytic combination of the $\mathrm{B}_\alpha^{+\bullet}$ and $\mathrm{H}^\bullet$ radicals, yielding a new $\mathrm{B}_\alpha\mathrm{H}^+$ chemical bond. Equation 4 immediately rationalizes some gross features of the PAs. It is common knowledge that proton affinities are appreciably higher than the average dissociation energy of covalent bonds, represented in eq 4 by $(\mathrm{BAE})_\alpha^+$. This is a consequence of the fact that $(\mathrm{IP})_1^{\mathrm{ad}} < \mathrm{EA}(\mathrm{H}^+)$ as a rule. Moreover, $-(\mathrm{IP})_1^{\mathrm{ad}}$ is the price in energy to be paid for the formation of a new bond. The lesser $(\mathrm{IP})_1^{\mathrm{ad}}$ the higher proton affinity, which in turn was built in the correlation between the PAs and the IPs.[9,10] It would be erroneous, however, to identify $(\mathrm{IP})_1^{\mathrm{ad}}$ values with properties of the initial base itself, because the adiabatic ionization potential involves the relaxation of both the electronic and geometric structures upon ionization. To delineate the initial state from the final state effect, one has to rely on Koopmans' theorem.[11] The latter states that the ionization potential $(\mathrm{IP})_n^{\mathrm{Koop}}$ is equal to the negative of the orbital energy $-\epsilon_n$ of a neutral molecule in its ground state, if the single-determinant approximation is employed. Moreover, it can be shown that Koopmans' theorem ensures the best description of ionization within the independent electron picture.[11,12] Consequently, $(\mathrm{IP})_n^{\mathrm{Koop}}$ will be calculated within the Hartree−Fock (HF) model. It is tacitly assumed that spatial and electronic structures are frozen during the ionization process, thus corresponding to the sudden approximation. Consequently, the calculated $(\mathrm{IP})_n^{\mathrm{Koop}}$ are related to the features of the electron density distribution in the initial bases.[12,13] Notice that $(\mathrm{IP})_n^{\mathrm{Koop}}$ does not necessarily correspond to the first ionization potential, because the lone pair electrons may correspond to MOs lower in energy than HOMO. In this context, it is useful to recall that Koopmans' theorem provides the interpretational basis of the photoelectron spectroscopy (PES), which in turn offers the most powerful experimental support to the one-electron MO picture of the electron distribution in molecules. It serves as an invaluable diagnostic tool in revealing intramolecular interactions between various functional groups within molecules.[13,14] It should be realized that relaxation of the structural parameters and the electron redistribution during and after the completion of the ionization event are parts of the protonation process. Thus they belong to the final state effects associated with the conjugate acids. Therefore, eq 4 should be rewritten in the following triad form:

$$(\mathrm{PA})_\alpha = -(\mathrm{IP})_n^{\mathrm{Koop}} + E(\mathrm{ei})_{\mathrm{rex}}^{(n)} + (\mathrm{BAE})_\alpha^+ + 313.6\ \mathrm{kcal/mol} \qquad (5)$$

where $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$ is conditionally termed as the relaxation energy upon the electron ejection:

$$E(\mathrm{ei})_{\mathrm{rex}}^{(n)} = (IP)_n^{\mathrm{Koop}} - (\mathrm{IP})_1^{\mathrm{ad}} \qquad (6)$$

Here $(\mathrm{IP})_n^{\mathrm{Koop}}$ and $(\mathrm{IP})_1^{\mathrm{ad}}$ refer to *n*th completely frozen state and to the first adiabatic ionization potential, respectively. It should be kept in mind that the contributions of the electron correlation energy in the calculation of $(\mathrm{IP})_1^{\mathrm{ad}}$ are not negligible. They are, however, lumped together with the electron density reorganization in the total relaxation energy $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$. In addition, it is important to realize that $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$ includes a difference between the adiabatic potentials $(\mathrm{IP})_n^{\mathrm{ad}} - (\mathrm{IP})_1^{\mathrm{ad}}$ if the ionized electron belongs to a MO_n, which is more stable than HOMO. Hence, the term relaxation energy is used in a broad general sense for the sake of simplicity. As a final comment we would like to strongly point out that dissection of the proton affinity embodied in eq 5 is somewhat arbitrary, although it gives in principle the exact PA value. The underlying assumption, that exactly one electron jumps from the lone pair to the incoming proton and forms H atom is of course an idealization. Nevertheless, it appears that it is pretty close to a realistic description of the net process. We shall come back to this point later on.

3. Computational Model

The theoretical model of choice should be simple, economical, and reliable. It is not easy to satisfy these contradictory requirements. Apparently, what has to be done is the best possible compromise between accuracy and practicality. Consequently, we shall optimize geometries at the B3LYP/6-31G* level, which is the simplest approach in taking into account the electron correlation effects. The protonation and the accompanying electron extraction from the nitrogen lone pair in our picture require the use of more flexible basis sets than the 6-31G* basis set. Our extensive computations have shown that the 6-311+G** basis set serves the purpose rather well within the MP2(fc) formalism for nitrogen protonation, where (fc) denotes that the inner-core electrons of heavy atoms are kept frozen during the Møller−Plesset perturbation calculation of the second order.[15] The Koopmans theorem ionization potential $(\mathrm{IP})_n^{\mathrm{Koop}}$ is computed by the HF/6-311+G**//B3LYP/6-31G* single-point, single-determinant model. Other entities are calculated by the restricted open shell ROMP2/6-311+G**//B3LYP/6-31G* model. We employed GAUSSIAN 94 and the GAMESS suite of programs[16,17] in the present work. The zero-point vibrational frequencies are obtained by the B3LYP/6-31G* procedure and were scaled by a common weighting factor 0.98 as is customary.[18]

4. Results and Discussion

4.1. Energetic Properties. Molecules examined in this study belong to the amine, imine, and phosphazene families. The second family of compounds involves also some polyfunctional amino-imines possessing several basic positions. Hydrogen cyanide is added to this set to extend the values of the s-character of local hybrid orbitals describing nitrogen lone pairs. Some of the studied molecules are depicted in Figure 1. Energetic data are presented in Table 1. Let us pinpoint some general conclusions, which can be derived from results displayed in Table 1. First, it is worth noting that the adiabatic ionization potentials are in good agreement with the experimental data[18] with very few exceptions. The same holds for computed proton affinities.[18] This high degree of accordance with experiment lends credence to the applied ROMP2(fc)/6-311+G**//B3LYP/6-31G* + ZPVE(B3LYP/6-31G*) model, which proved efficient and useful. Moreover, the proton affinities PA(5) obtained via eq 5 are in good accordance with results achieved by the MP2(fc)/6-311+G**//B3LYP/6-31G* + ZPVE(B3LYP/6-31G*) approach. The latter is a refined version of our earlier model, which gave very good agreement with available experimental data.[15] That model involved geometry optimization and calculation of ZPVEs at the simpler HF/6-31G* level. The present model will be abbreviated as MP2 and used within the standard definition of the proton affinity:

$$(\mathrm{PA})_\alpha = (\Delta E_{\mathrm{el}})_\alpha + (\Delta \mathrm{ZPVE})_\alpha \qquad (7)$$

Here $(\Delta E_{\mathrm{el}})_\alpha = E(\mathrm{B}) - E(\mathrm{B}_\alpha\mathrm{H})^+$ and $(\Delta\mathrm{ZPVE})_\alpha = \mathrm{ZPVE(B)} - \mathrm{ZPVE}(\mathrm{B}_\alpha\mathrm{H})^+$ are electronic and the zero-point vibrational energy contributions to the proton affinity, respectively. Although both models employed in connection with eqs 5 and 7 are very close as far as their levels of sophistication are concerned, strictly speaking they are different. Hence, some differences in the calculated PAs can be expected. It is gratifying that they are small in most cases. As a final remark we would like to mention that experimental PAs[19,20] are quoted wherever possible. If they were lacking, we used G2(MP2) values as reference values. The G2(MP2) results were either taken from the literature or were obtained by us in this work.

We begin discussion with results obtained for ammonia and its alkylated derivatives $\mathrm{NH}_{3-m}(\mathrm{R})_m$ ($m = 0-3$), where R stands for $\mathrm{CH_3}$ or $\mathrm{C_2H_5}$. An important feature of this series of compounds is that they have only one unshared pair of electrons, which is placed in the HOMO (Figure 2). Therefore, $(\mathrm{IP})_n^{\mathrm{Koop}}$ refers to the first ionization potential ($n = 1$). It is useful to develop a feeling about the order of magnitude of various terms in eq 5. It appears that stabilization induced by the electron transfer from the lone pair to the proton measured by $[313.6 - (\mathrm{IP})_1^{\mathrm{Koop}}]$ kcal/mol increases in the series $\mathrm{NH}_{3-m}(\mathrm{Me})_m$ ($m = 0-3$) from 43.3 to 92.4 kcal/mol. In contrast, the bond association energy decreases from 119.0 to 91.7 kcal/mol. Both contributions become about the same in $\mathrm{NMe_3}$. These two trends are intuitively clear. If the lone pair is less tightly bound and the price for ionization is smaller, the energy gain upon formation of a new N−H bond is less beneficial and thus corresponds to a stockholder principle: less investment, less profit. This conclusion is correct, however, qualitatively but not quantitatively.

The relaxation energy is practically constant being 41 kcal/mol, which is perhaps the most striking finding offered by the numerical analysis obtained from eq 5. It exhibits, though, a mild increase in $\mathrm{NH(Et)_2}$ and $\mathrm{N(Et)_3}$, assuming values 43.6 and 46.8 kcal/mol, respectively. This somewhat surprising constancy of the relaxation effect is in contradiction with the general notion that the polarizability of a molecule increases with a number of the alkyl groups. It is, therefore, of some interest to examine the relaxation energy in more detail. In fact, it has two contributions related to orbital and nuclear relaxation. The former is given by $(\mathrm{IP})_1^{\mathrm{Koop}} - (\mathrm{IP})_1^{\mathrm{v}}$, while the latter is defined by $(\mathrm{IP})_1^{\mathrm{v}} - (\mathrm{IP})_1^{\mathrm{ad}}$, where $(\mathrm{IP})_1^{\mathrm{v}}$ stands for the first vertical ionization potential. Their sum yields $E(\mathrm{ei})_{\mathrm{rex}}^{(1)}$, as required. The vertical ionization potentials $(\mathrm{IP})_1^{\mathrm{v}}$ are calculated by using the geometry of the ground-state kept frozen during the ionization event. The molecular orbitals of the radical cation are optimized, however, within this constraint. It appears that the relaxation of MOs yields reorganization energies, which span a range between 22.1 and 25.6 kcal/mol in a series $\mathrm{NH}_{3-m}(\mathrm{Me})_m$, ($m = 0-3$). The corresponding orbital relaxation energies in a series $\mathrm{NH}_{3-m}(\mathrm{Et})_m$ ($m = 0-3$) are higher and increase in the range 22.1−29.5 kcal/mol. Consequently, orbital relaxations are compatible with the idea that they should be more pronounced with the size of alkyl groups and their number.

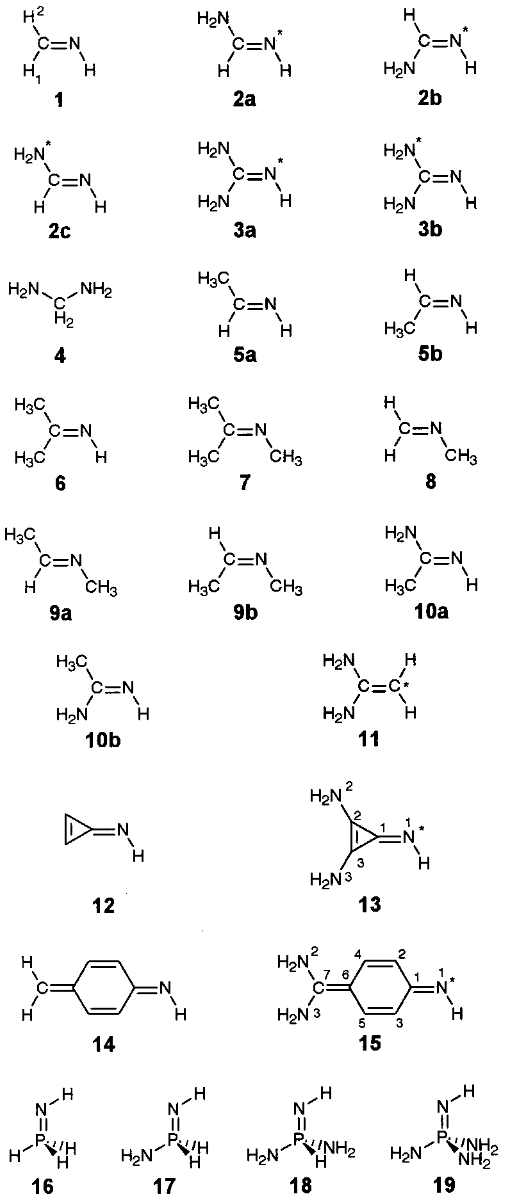

Figure 1. Schematic representation of amines and phosphazenes involving imino and amino basic centers. The protonated atom is denoted by an asterisk.

Another point of interest is the relaxation energy during the homolytic N−H bond formation. For this purpose we calculated the bond association energy $(\mathrm{BAE})_{\mathrm{frc}}^{+\bullet}$, where the subscript frc denotes the frozen radical cation structure, and optimized only the N*−H bond distance. Here and elsewhere an asterisk denotes the protonated nitrogen atom. The difference between $(\mathrm{BAE})^+ - (\mathrm{BAE})_{\mathrm{frc}}^{+\bullet}$ gives the relaxation effect, which describes a change in energy between the instantaneous N*−H

TABLE 1: Calculated Koopmans' and Adiabatic Ionization Potentials and Comparison of the Latter with Experimental Data (all entries in kcal/mol)

system	$(IP)_1^{ad}$	$(IP)_{exp}^{ad}$	$(IP)_n^{Koop,a}$	$E(ei)_{rex}^{b}$	$(BAE)^{+\,b}$	$PA(5)^{b}$	PA^{c}
NH_3	229.5	232.2 ± 0.5	$(270.3)_1$	40.8	119.0	203.1	204.1 [204.0]
$NH_2(Me)$	205.5	205.2 ± 2.3	$(246.3)_1$	40.8	106.4	214.5	214.6 [214.9]
$NH(Me)_2$	191.4	190.0 ± 1.8	$(231.4)_1$	40.0	97.9	220.1	221.6 [222.2]
$N(Me)_3$	180.3	181.0 ± 1.2	$(221.2)_1$	40.9	91.7	225.0	226.0 [226.8]
$NH_2(Et)$	204.5	205.2	$(245.4)_1$	40.9	106.1	215.2	217.2 [218.0]
$NH(Et)_2$	186.6		$(230.2)_1$	43.6	98.2	225.2	226.2 [227.2]
$N(Et)_3$	171.3	173.6 ± 2.3	$(218.1)_1$	46.8	90.5	232.8	232.9 [234.7]
1	230.6	229.9	$(271.7)_1$	41.0	120.6	203.6	205.8 [203.8]
2a	212.2		$(267.6)_2$	55.1	121.7	223.2	224.3 $[225.4]_{G2(MP2)}$
2b	209.9		$(269.7)_2$	59.8	121.7	225.5	226.5
2c	212.2		$(233.5)_2$	21.2	93.4	194.9	194.1 $[195.8]_{G2(MP2)}$
3a	198.1		$(267.7)_2$	69.5	116.4	232.0	233.2 [235.7]
3b	198.1		$(231.6)_2$	33.5	84.1	199.7	200.8 $[200.7]_{G2(MP2)}$
4	214.2		$(244.0)_1$	29.8	95.5	218.7	219.2 $[218.9]_{G2(MP2)}$
5a	222.1	221.3	$(265.2)_1$	43.1	120.5	212.1	214.3 [211.5]
5b	246.7		$(264.5)_1$	17.8	147.5	214.4	215.4
6	213.8	198.3	$(259.4)_1$	45.6	120.4	220.3	222.1 [222.8]
7	195.3	200.6	$(241.2)_1$	45.9	109.3	227.7	228.9
8	212.2	214.5	$(257.4)_1$	45.2	109.9	211.4	213.3 [211.4]
9a	205.2	207.5	$(251.4)_2$	46.2	110.6	219.0	220.6
9b	201.1		$(245.1)_1$	44.0	109.2	221.7	223.0
10a	203.6		$(261.8)_2$	58.2	119.3	229.3	230.5 [232.0]
10b	202.5		$(265.2)_2$	62.7	119.3	230.4	231.5
11	167.4		$(193.9)_1$	26.5	94.5	240.7	241.2 [242.0]
$H-C\equiv N$	314.8	313.6	$(366.1)_3$	51.3	168.4	167.2	168.4 [170.4]
12	204.8		$(243.1)_2$	38.3	118.3	227.1	229.8 $[229.5]_{G2(MP2)}$
13	172.5		$(236.6)_2$	64.1	108.0	249.1	249.8 $[250.9]_{G2(MP2)}$
14	188.4		$(267.7)_3$	79.3	107.0	232.2	233.9
15	150.1		$(249.1)_3$	99.0	101.8	265.3	265.5
16	231.5		$(256.0)_2$	24.5	148.5	230.6	231.3 $[225.8]_{G2}$
17	195.3		$(250.8)_2$	55.5	116.5	234.8	233.8 $[233.8]_{G2}$
18	190.0		$(251.8)_2$	61.8	116.2	239.8	242.4 $[241.0]_{G2}$
19	183.3		$(250.3)_2$	67.0	117.0	247.3	248.5 $[247.8]_{G2}$

[a] $(IP)_n^{Koop}$ refers to Koopmans' ionization potentials for ionization of an nitrogen lone pair. Index n stands for HOMO − $(n-1)$ molecular orbital. [b] Definition of the relaxation energy $E(ei)_{rex}$ upon ionization and the bond association energy between the radical cation and hydrogen $(BAE)^+$ are described in the text. The proton affinity PA(5) is obtained via eq 5. [c] PA denotes the proton affinity computed by the MP2 model and eq 7. Experimental and G2(MP2) results are given within square parentheses. G2(MP2) and G2 calculations are carried out in this work except results for molecules **10b** and **11**, which were taken from ref 31.

bond formation and a subsequent readjustment of the electrons and nuclei of the radical cation. This type of the relaxation is relatively large in methylamines assuming values 22.5, 26.6, 36.5, and 41.0 kcal/mol in the sequence NH_3, NH_2CH_3, $NH(CH_3)_2$, and $N(CH_3)_3$, respectively, thus exhibiting increases compatible with expectation. It is important to note that Koopmans' ionization potentials undergo a faster decrease than the homolytic bond association energies $(BAE)^+$ along each of these two series, thus leading to appreciable amplification of basicity with a number of either CH_3 or C_2H_5 groups. Moreover, it appears that $(IP)_1^{Koop}$ is slightly smaller and $E(ei)_{rex}$ is slightly larger in ethyl derivatives than in the corresponding methyl derivatives. Hence, it can be concluded that larger alkyl groups lead to larger PAs and stronger basicities. It can be also safely

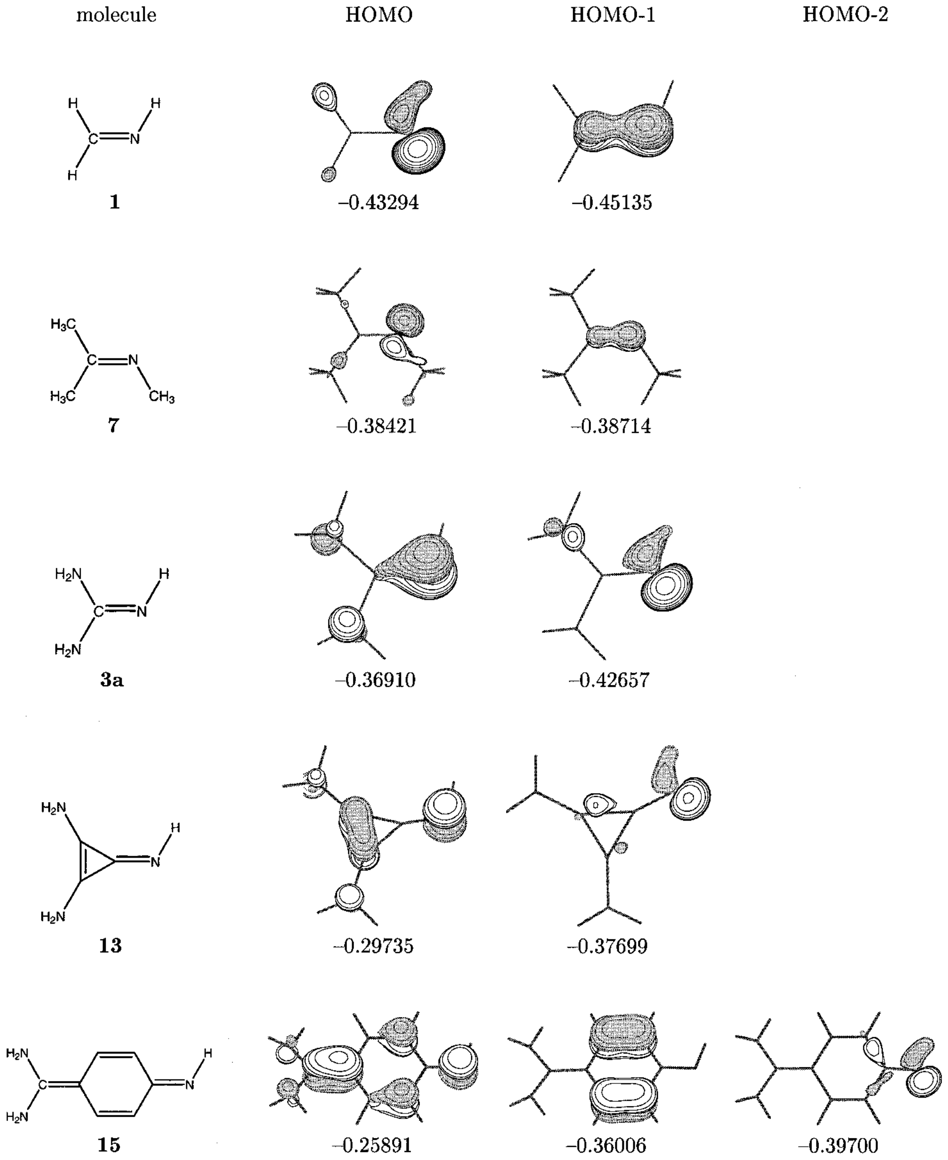

Figure 2. Pictorial representation of HOMO, HOMO-1, and HOMO-2 molecular orbitals in some characteristic molecules. The proton target is the lone pair orbital.

stated that the basicity in series $NH_{3-m}R_m$ (where $m = 0-3$ and $R{=}CH_3$, C_2H_5) in the gas phase is determined by the ground-state properties of initial bases. More specifically, the electron donating abilities, mirrored by $-(IP)_1^{Koop}$ values, prevail over other effects related to the resulting conjugate acids. There are two different possible mechanisms yielding to smaller $(IP)_1^{Koop}$ ionization potentials with increased alkyl substitution. One is the hyperconjugative interaction between the lone pair hybrid orbital and the pseudo-π semilocalized orbital of the methyl or ethyl groups. The second possible source is given by a fact that the hybridization s-character of the lone pair decreases as the number of alkyl substituents increases (vide infra).

It is interesting to compare our findings with results of Fujimoto et al.,[21] who treated the protonation of ammonia and its methyl derivatives in the way proposed by Mulliken in his charge-transfer theory of complexes.[22] For instance, the electron distribution in protonated ammonia is described as a mixture of two configurations specified by the ($NH_3 + H^+$) and ($NH_3^+ + H$) situations. Performing some specific MO transformations Fujimoto et al.[21] arrive at an index γ, which yields the electron donating ability of ammonia and its CH_3 derivatives. It turned out that γ values correlated very well with the experimental PAs or, in other words, basicity of methylated amines were determined by the electronic features of initial bases. Hence, their conjecture is in qualitative agreement with results of our analysis.

Recently, much research interest has been focused on some simple imines,[23] polyfunctional formamidines[24] and cyclic and acyclic guanidines,[25] with the idea of extending the basicity scale to the upper limit values. Imines considered here can be divided into several subsets. The first is encompassed by amino imines starting with the parent compound methyleneimine **1** (Figure 1). The HOMO in this molecule is the lone pair orbital, but an inversion occurs in formamidine **2a** and guanidine **3a**, where the lone pair orbital energy is shifted below the C=N π-double bond, i.e., it becomes HOMO-1. Since the protonation takes place in the plane of the molecular skeleton in the direction of the maximum electron density of the lone pair, we deemed it appropriate to take into account $(IP)_2^{Koop}$ as a price to be paid in forming a new N−H bond with the incoming proton. Although a drift of the electron density to the proton does not strictly correspond to a complete ionization, i.e., ejection of one electron to infinity, as assumed in our idealized picture, we feel that the relaxation energy $E(\mathrm{ei})_{\mathrm{rex}}^{(2)} = (\mathrm{IP})_1^{\mathrm{ad}} - (\mathrm{IP})_2^{\mathrm{Koop}}$ describes much of the stabilization arising from reorganization upon the creation of a new NH chemical bond. The most striking feature of changes of various terms in a series **1**, **2a**, **3a** is a dramatic increase in $E(\mathrm{ei})_{\mathrm{rex}}$ between the parent compound **1** and guanidine **3a** being as large as 28.5 kcal/mol. This is exactly the difference between PAs of these two molecules (Table 1). Obviously, amplification of the basicity of **1** upon mono- and diamination is a final state effect. This result is in full harmony with our earlier conclusion that a very effective cationic resonance interaction in conjugate acids in guanidine and higher polyguanides is the reason behind their strong basicity.[26] It is particularly satisfying that the same conclusion is reached by two completely different lines of thought: the first is deduced by eq 5, whereas the second follows from a use of appropriate homodesmic reactions.[26] The same holds for extended π-systems involving guanidine and cyclopropeneimine subunits.[27] Hence, conjecture of Gobbi et al.[28] that the high basicity of guanidine is a consequence of a strong hydrogen bonding of guanidine cation in solution cannot be excluded, but should be taken with due caution. Our analysis convincingly shows that guanidine is genuinely a very basic compound, with its basicity predominantly determined by the conjugate acid. The solvent effect of guanidine in acetonitrile will be considered in section 5.

An interesting pair of molecules is given by isomers **2a** and **2b**. They result in the same conjugate acid, implying that a less stable isomer is the more basic one, which is **2b**. One is tempted to conclude, therefore, that the higher basicity is determined by the initial state of **2b**. In a way, this seems to be correct at the first sight, but analysis presented in Table 1 shows that **2b** has larger relaxation energy, which ultimately leads to a slightly higher proton affinity. Hence, the latter is a consequence of the final state, because a less stable isomer has to be more stabilized to arrive at the same conjugate acid, meaning that it is more basic. This example illustrates some conceptual difficulties in discriminating initial and final state effects.

Another illustrative case is provided by the paradigmatic proton sponge 1,8-(bis)-dimethylaminonaphthalene (DMAN).[29,30] It is well recognized that the repulsion of the lone pairs in DMAN is a feature that ultimately leads to a pronounced basicity of this compound. However, the unfavorable interaction in the initial base is relieved in the protonation process, which ultimately results in a rather strong intramolecular hydrogen bond. This is clearly a final-state effect. It follows that the electronic (and structural) features of bases are usually very closely related to those of conjugate acids and in fact they determine the latter. In other words, conjugate acids "remember" structural and electronic patterns of their conjugate bases albeit sometimes in a disguised form. Consequently, a sharp borderline between the initial and final state effects cannot always be drawn. It should be kept in mind that distinction between the initial and final state effects is meaningful only within the context of eq 5, if it is adopted by convention.

An important issue is a preference of one basic site over another in the same polyfunctional base. Let's discuss the difference in the proton affinities of $H_2NCH{=}N^*H$ (**2a**) and $H_2N^*CH{=}NH$ (**2c**), where the protonated nitrogens are denoted by an asterisk. According to $(\mathrm{IP})^{\mathrm{Koop}}$ ionization potentials, the protonation at the sp^3 lone pair of the amine group should be more profitable by 34 kcal/mol. However, the sp^2 imine nitrogen is more basic as revealed by the difference PA(**2a**) − PA(**2c**) = 28.3 kcal/mol (Table 1). The origin of the greater susceptibility of imine nitrogen toward protonation is identified as a much larger relaxation effect, $\Delta E(\mathrm{ei})_{\mathrm{rex}} = 34$ kcal/mol, and a considerably stronger N*−H bonding by 28.3 kcal/mol. It follows, somewhat fortuitously, that the unfavorable ionization and favorable relaxation energy completely cancel out. The end effect is that PA(**2a**) − PA(**2c**) = $E(N^*(sp^2)\text{-}H) - E(N^*(sp^3)\text{-}H)$, meaning that $N(sp^2)$-H bond energy is larger than $N(sp^3)$-H bond energy, which is in harmony with the concept of hybridization and with the calculated bond association energies $(\mathrm{BAE})^+$s. One concludes that greater basicity of imine over amine nitrogen in formamidine is pure final state effect. It should be stressed that one cannot say that the imine nitrogen is more basic than the amine nitrogen in general, because, e.g., NH_3 and **1** have practically the same proton affinity. However, this appears to be true for compounds considered here, alkylated amines and diaminomethane **4** being notable exceptions. Finally, let us consider the protonation of NH_2 group in guanidine and compare it with that in **2c**. It involves ionization from a somewhat higher HOMO, which is followed by a concomitant formation of a weaker NH bond relative to **2c** (Table 1). However, there is an increase in the relaxation energy by 12.3 kcal/mol, which ultimately leads to amplified PA by 4.8 kcal/mol compared to **2c** as the bottom line.

Methylation of **1** deserves some more attention. Substitutions of CH_3 groups at carbon and nitrogen atoms are clearly distinguished. The former shifts the HOMO in **5a** up, which is further enhanced by the double substitution in **6** and triple substitution in **7**, relative to **1** by 6.5, 12.3, and 30.0 kcal/mol, respectively. Apparently, the substitution at nitrogen is more effective as intuitively expected. Since the corresponding shift in **8** is 14.3 kcal/mol, one concludes that the CH_3 substituent effect on the $(\mathrm{IP})^{\mathrm{Koop}}$ is roughly additive. The same holds for the PA, which increases along the series **1**, **5a**, **6**, and **7** by approximately 8 kcal/mol. Obviously, the basicity in the gas phase is determined by the initial base features. A sharp decrease in the homolytic bond association energy in **7** can be rationalized by the rehybridization effect (vide infra). The approximate additivity works also in the series **1**, **8**, **9a** (or **9b**), and **7**. We arrive at the interesting conclusion that amination of **1** leads to basicities governed by the final-state effects as shown earlier, whereas the opposite is true for alkylation, where the initial-state effects are decisive. It is therefore of some interest to examine systems **10a** and **10b** involving both CH_3 and NH_2 substituents. The lone pair of the imino nitrogen is placed in HOMO-1 orbital in both compounds, implying that $(\mathrm{IP})_2^{\mathrm{Koop}}$ is required. The additivity of individual contributions of CH_3 and NH_2 groups would yield the PA of 234.0 kcal/mol for **10b**, which compares fairly well with the actual value 231.5 kcal/mol. It is noteworthy that **10b** takes over the $(\mathrm{IP})^{\mathrm{Koop}}$ from **5a** and the relaxation energy from **2b**, whereas the bond association energy is roughly the same in all three compounds. To put it another way, **10b** combines favorable features of both CH_3 and NH_2 substituent effects achieving a relatively high proton affinity of 230.4 kcal/mol. An even more pronounced basicity is obtained for 1,1-diaminoethylene **11**, which has a proton affinity higher than **10b** by 10 kcal/mol as already noticed by Yañez et al.[31] However, it is interesting that in this case the most basic site is the unsubstituted carbon atom and that HOMO is the π-orbital of the double bond. Results given in Table 1 show that the origin of the increased basicity of **11** can be identified as a very low first Koopmans' ionization potential of 193.9 kcal/mol. This means that ionization is less costly than that in **10b** by 71.3 kcal/mol! Hence, the proton affinity undergoes an increase relative to PA(**10b**), despite appreciably lower relaxation and smaller homolytic C*−H bond association energy. It follows that the proton affinity of **11** is predominantly a consequence of an initial-state effect.

Hydrogen cyanide is a perfect illustration of the importance of the hybridization effect. It has a very low basicity because of the strongly bound sp^1 lone pair, as evidenced by the very high $(IP)_3^{Koop}$ ionization potential being 366.1 kcal/mol. The ionization from this level is so unfavorable that it cannot be remedied by a higher relaxation energy (by 10 kcal/mol) and considerably stronger bond energy $(BAE)^+$ (by 49 kcal/mol) compared to situations occurring in both NH_3 and $H_2C{=}NH$. As a result HCN is a very weak base.

A particularly interesting set of molecules is given by cyclic compounds **12**−**15**. According to our earlier studies, these compounds exhibit amplified basicities due to aromatization triggered by protonation.[15] This effect is particularly strong in cyclopropeneimine and quinoneimine rings, if substituted by NH_2 groups at important strategic positions, such as in **13** and **15**. The imino lone pairs in these molecules are described by HOMO-1 and HOMO-2, respectively (Figure 2). The corresponding relaxation energies are 64.1 and 90.0 kcal/mol. However, these favorable reorganization effects are diminished by weaker N*(sp^2)−H bonds by −11.0 and −17.2 kcal/mol, respectively, relative to NH_3. Moreover, since lone pair electrons of imino nitrogens in **13** and **15** are less tightly bound by −33.7 and −21.2 kcal/mol, respectively, again relative to NH_3, as evidenced by $(IP)^{Koop}$ values, it follows that the corresponding amplification in the PAs can be ascribed 73% and 34% to the initial state effects, if NH_3 (or $H_2C{=}NH$) is taken as the origin of the PA scale. Obviously, their high basicity is determined by an interplay of the initial state and final state properties. The latter are predominantly influenced by large relaxation effects. A word about low $(IP)_n^{Koop}$ ($n = 2, 3$) values despite very high lone pair s-characters is in order. It is a consequence of a strong interaction of the lone pair hybrid AO with Walsh orbitals[32] of the three-membered ring in **13**. This has some structural consequences too, as it will be discussed in section 4.2. Obviously a similar interaction with quinoid ring occurs in **15**.

It is well understood that polyaminophosphazenes are the most potent neutral bases.[33] Concomitantly, we felt it worthwhile to examine the first simplest mono- and polyaminophosphazenes **16**−**19**. Despite the fact that phosphazenes are considered in the literature as compounds involving pentavalent phosphorus, which implies a double bond between phosphorus atom and imine nitrogen, calculations show that the electron density of the double bond is almost exclusively concentrated on the nitrogen π−AO. Hence, the double bond is highly polar, being better described as $P^+{-}N^-$ charge distribution. In other words, nitrogen has practically two lone pairs. The proton affinity steadily increases along the series **16**−**19** with a number of amine groups. Increments per amine group are in the range of 4−8 kcal/mol. The simplest and the least basic compound is monophosphazene **16**. Compared to iminoethene **1**, monophosphazene **16** derives its increased proton affinity from a lower $(IP)^{Koop}$ potential (by −15.7 kcal/mol) and much stronger bond association energy $(BAE)^+$ (by 28 kcal/mol), presumably because of the high electron density concentration on the imine nitrogen due to a substantial negative charge drift from P to N as mentioned above. Surprisingly, the relaxation energy in **16** is appreciably smaller than in the simplest imine **1** by −16.5 kcal/mol. It appears that 58% of the increase in the PA (relative to **1)** phosphazene **16** is owed to the initial state effect. The corresponding initial state participation in the enhancement of the PA along **17**−**19** group of compounds, taking **1** as the origin of the PA scale, assumes 67%, 55%, and 49%, respectively. Apparently, the trend of changes in the basicity of phosphazenes is dictated by an interplay between the initial- and final-state effects. As a final comment we would like to point out that the relaxation effect in polyaminophosphazenes increases with a number of NH_2 substituent groups as intuitively expected. It is important to stress that, if we are interested in contributions of the initial and final states in absolute sense for each particular phosphazene in the series **16**−**19**, then analysis performed by using data in Table 1 and eq 5 shows that the initial state is responsible for approximately 25% of the PA values only.

4.2. Geometries and Bonding Parameters. Bond distances for some typical molecules and their relaxed radical cations as well as for protonated forms are displayed in Table 2. We provide also the s-characters of local hybrid orbitals, which possess a high interpretive content,[34] meaning that they are able to rationalize a number of local molecular properties. Here we utilize the hybrid orbitals and their parameters retrieved from the molecular wave functions by the natural bond orbital analysis.[35] Another important piece of information is given by atomic charges, which offer an insight into the redistribution of the electron density upon the chemical bond formation or in this case upon protonation. Neither s-characters[34] nor formal atomic charges[36] have an absolute meaning, but they are usually useful in considering trends of changes of some properties along a series of related compounds, provided other effects remain reasonably constant. We shall make use of Mulliken charges[37] obtained by equipartition of mixed electron densities between atoms and Löwdin charges deduced by the symmetric orthogonalization of atomic orbitals, which in turn appropriately transform the already computed molecular wave function employing the overlapping basis set.[38] It is well known that Mulliken partitioning overemphasizes the intramolecular charge transfer, whereas Löwdin analysis minimizes the charge drift.[36] The latter have also some other conceptual advantages and, consequently, they are generally considered as more reliable.

Let us focus again on the $NH_{3-n}(Me)_n$ series first. Removal of an electron from the lone pair leads to planar radical cations. Union of the latter with hydrogen atom reestablishes the earlier tetrahedral, or better to say, earlier deformed tetrahedral, spatial structures. This is a consequence of the fact that formation of the homolytic N−H bond brings the ejected electron back to the valence electron shell of a molecule. Concomitantly, the former geometry is approximately restored and the hybridization s-characters of initial bases are recovered to a large extent.

Perusal of changes in the s-characters for $NH_{3-n}R_n$ ($n = 0{-}3$) series, where R = CH_3, C_2H_5, shows that the s-content of the lone pair decreases as the number of alkyl groups is increased. This implies that the lone pair electron is more loosely bound, which results in a fairly good linear relationship between the s-characters and the $(IP)_1^{Koop}$ ionization potentials

$$(IP)_1^{Koop} = 4.32s(\%) + 155.8 \text{ kcal/mol} \qquad (8)$$

with a regression coefficient $R^2 = 0.95$ and the average absolute error $\Delta(IP)_1^{Koop} = 3.2$ kcal/mol. The trend of changes is qualitatively correct and intuitively clear, but the relatively low quality of the correlation, as evidenced from high average absolute deviations and small regression coefficient, indicates that other effects such as hyperconjugative interactions might be operative too. Similarly, there should be a linear relation between the s-character of the new N*−H bond and the bond association energy. Namely, it is well established that the bond strength is linearly related to the overlap integrals,[34] which in turn are proportional to the s-content of hybrid AOs. Calcula-

TABLE 2: Bond Distances (in Å), Hybrid s-characters (in %), and Atomic Charges (in |e|)

					charge^a							charge^a	
molecule	bond	dist	s-character	atom	M	L	molecule	bond	dist	s-character	atom	M	L
NH$_3$	N−H	1.019	25.0	N	−0.68	−0.40	13	N1=C1	1.282	38.9−43.0	N1	−0.60	−0.37
(NH$_3$)$^{+\bullet}$		(1.029)	(33.2)		(−0.13)	(0.30)	(13)$^{+\bullet}$		(1.304)	(35.8−40.1)		(−0.19)	(0.01)
[NH$_4$]$^+$		[1.029]	[25.0]		[−0.45]	[0.11]	[13H]$^+$		[1.329]	[38.6−38.3]		[−0.59]	[−0.12]
	lp		25.0	H	0.23	0.13		C1−C2	1.437	29.6−29.9	C1	0.23	0.03
			(0.0)		(0.38)	(0.23)			(1.420)	(30.9−31.1)		(0.04)	(−0.01)
					[0.36]	[0.22]			[1.384]	[30.7−30.7]		[0.27]	[0.07]
NH$_2$(Me)	N−C	1.465	32.0−26.9	N	−0.52	−0.33		C1−C3	1.425	27.1−30.3	C2	0.08	−0.05
(NH$_2$(Me))$^{+\bullet}$		(1.420)	(40.5−23.5)		(−0.04)	(0.23)			(1.410)	(28.7−31.4)		(0.32)	(0.09)
[NH$_3$(Me)]$^+$		[1.518]	[31.1−20.9]		[−0.39]	[0.07]			[1.384]	[30.7−30.7]		[0.27]	[0.07]
	N−H	1.019	23.2	C	−0.23	−0.18		C2=C3	1.350	33.9−33.3	C3	0.14	−0.03
		(1.025)	(29.8)		(−0.32)	(−0.11)			(1.406)	(30.2−29.6)		(0.35)	(0.10)
		[1.028]	[23.2]		[−0.25]	[−0.08]			[1.384]	[30.7−30.7]		[0.27]	[0.07]
	lp		21.6	H(N)	0.22	0.13		C2−N2	1.375	35.9−35.8	N2	−0.53	−0.19
			(0.0)		(0.35)	(0.22)			(1.315)	(38.4−39.6)		(−0.55)	(−0.09)
					[0.35]	[0.21]			[1.329]	[38.2−38.8]		[−0.59]	[−0.12]
				H(C)	0.11	0.09		C3−N3	1.370	36.1−36.0	N3	−0.54	−0.18
					(0.21)	(0.14)			(1.313)	(38.7−39.4)		(−0.56)	(−0.08)
					[0.20]	[0.13]			[1.329]	[38.3−38.6]		[−0.59]	[−0.12]
NH(Me)$_2$	N−C	1.457	30.7−26.4	N	−0.33	−0.29		N(1)−H	1.024	21.3	H(N1)	0.18	0.13
(NH(Me)$_2$)$^{+\bullet}$		(1.438)	(36.9−23.4)		(0.03)	(0.16)			(1.026)	(21.7)		(0.26)	(0.18)
[NH$_2$(Me)$_2$]$^+$		[1.510]	[29.3−21.4]		[−0.33]	[0.03]			[1.010]	[30.7]		[0.32]	[0.19]
	N−H	1.018	21.1	C	−0.26	−0.19		lp		39.8			
		(1.024)	(26.2)		(−0.30)	(−0.12)				(42.4)			
		[1.027]	[20.8]		[−0.25]	[−0.11]	15	N1=C1	1.299	41.2−34.1	N1	−0.42	−0.30
	lp		17.7	H(N)	0.22	0.13	(15)$^{+\bullet}$		(1.335)	(37.6−31.0)		(−0.17)	(−0.06)
			(0.0)		(0.34)	(0.20)	[15H]$^+$		[1.351]	[41.0−29.6]		[−0.56]	[−0.17]
					[0.34]	[0.20]		C1−C2	1.464	33.8−33.5	C1	−0.18	−0.01
				H(C)	0.11	0.10			(1.437)	(35.1−34.2)		(−0.26)	(−0.04)
					(0.20)	(0.15)			[1.420]	[35.0−33.9]		[0.17]	[0.08]
					[0.19]	[0.13]		C1−C3	1.462	31.8−33.8	C2	0.02	−0.16
N(Me)$_3$	N−C	1.455	28.7−25.7	N	−0.11	−0.29			(1.436)	(33.5−33.9)		(0.14)	(−0.09)
(N(Me)$_3$)$^{+\bullet}$		(1.450)	(33.3−23.6)		(0.15)	(0.07)			[1.420]	[35.1−33.9]		[−0.04]	[−0.14]
[NH(Me)$_3$]$^+$		[1.507]	[27.2−21.8]		[−0.30]	[−0.03]		C2=C4	1.356	38.1−38.5	C3	0.02	−0.13
	N−H	- -	- -	C	−0.29	−0.19			(1.378)	(36.6−37.0)		(0.09)	(−0.06)
		(- -)	(- -)		(−0.32)	(−0.12)			[1.377]	[36.8−37.1]		[−0.01]	[−0.14]
		[1.026]	[18.5]		[−0.26]	[−0.11]		C3=C5	1.354	37.9−38.6	C4	−0.70	−0.07
	lp		14.1	H(N)	- -	- -			(1.378)	(36.3−37.0)		(−0.72)	(−0.06)
			(0.0)		(- -)	(- -)			[1.377]	[36.8−37.1]		[−0.68]	[−0.03]
					[0.34]	[0.19]		C4−C6	1.446	33.8−32.8	C5	−0.66	−0.08
				H(C)	0.11	0.10			(1.417)	(34.2−35.1)		(−0.68)	(−0.06)
					(0.20)	(0.15)			[1.416]	[34.5−34.6]		[−0.68]	[−0.03]
					[0.19]	[0.13]		C5−C6	1.449	33.6−32.9	C6	1.52	−0.20
1	N=C	1.270	41.5−37.5	N	−0.32	−0.25			(1.417)	(34.2−35.2)		(1.21)	(−0.13)
(1)$^{+\bullet}$		(1.235)	(52.2−34.2)		(0.01)	(0.18)			[1.416]	[34.5−34.6]		[1.21]	[−0.18]
[1H]$^+$		[1.279[	[41.2−34.2]		[−0.25]	[0.03]		C6=C7	1.388	34.2−42.0	C7	−0.38	0.06
	N−H	1.027	20.7	C	−0.11	−0.07			(1.463)	(29.6−37.7)		(0.10)	(0.17)
		(1.024)	(45.8)		(0.03)	(0.18)			[1.444]	[30.8−38.6]		[0.04]	[0.16]
		[1.022]	[29.4]		[0.07]	[0.21]		C7−N2	1.382	28.9−37.3	N2	−0.47	−0.20
	C−H1	1.099	32.6	H(N)	0.19	0.13			(1.332)	(31.0−40.2)		(−0.49)	(−0.11)
		(1.107)	(33.4)		(0.41)	(0.26)			[1.339]	[30.6−40.2]		[−0.49]	[−0.12]
		[1.088]	[33.1]		[0.35]	[0.22]		C7−N3	1.382	28.9−37.3	N3	−0.47	−0.20
	C−H2	1.094	30.4	H1	0.11	0.09			(1.332)	(31.0−40.2)		(−0.49)	(−0.11)
		(1.101)	(32.8)		(0.27)	(0.19)			[1.339]	[30.6−40.2]		[−0.49]	[−0.12]
		[1.088]	[33.1]		[0.24]	[0.16]		N(1)−H	1.027	20.9	H(N1)	0.19	0.13
	lp		37.9	H2	0.13	0.10			(1.028)	(21.2)		(0.24)	(0.16)
			(1.9)		(0.27)	(0.19)			[1.009]	[29.4]		[0.31]	[0.18]
					[0.24]	[0.16]		lp		37.8			
										(41.1)			

[a] Mulliken and Löwdin atomic charges are denoted by (M) and (L), respectively.

tions show that there is indeed a linear relation valid for both CH_3 and C_2H_5 derivatives of ammonia $(NH_{3-m}R_m)^+$ taken together

$$(\mathrm{BAE})^{+}_{\mathrm{NH}} = 4.03s(\%) + 15.7\ \mathrm{kcal/mol} \qquad (9)$$

where $s(\%)$ is related to the formed N*−H bond. The average absolute error $\Delta(\mathrm{BAE})^+ = 1.4$ kcal/mol and $R^2 = 0.97$. Consequently, the trend of changes in the bond association energies along both series can be at least qualitatively rationalized by the rehybridization argument.

The lone pair in methyleneimine **1** has an s-character close to the sp^2 canonical value (37.9%). One would, therefore, expect that the Koopmans ionization potential is substantially higher than in NH_3. Surprisingly enough, it is larger by only 2.4 kcal/mol. One is tempted to conclude that there is a through-space interaction between the lone pair and C−H bond. This is borne out by structural parameters of **1** presented in Table 2.

Interaction of the unshared electron pair with its vis-à-vis C−H(1) bond pushes the latter away by a slight increase in the bond distance and by substantial enlargement of the corresponding H(1)−C═N angle to 125.7°. This finding indicates that rehybridization is a good model only for closely related molecules, which do not differ dramatically in their spatial and electronic structure. A very important point is, however, that hybrid AOs provide an extremely useful basis for considering intramolecular interaction as shown inter alia by Heilbronner et al.[13] and by us.[34] Therefore, they provide groundwork for building up more refined and powerful but still simple models. Methyl substitution at nitrogen in **8** diminishes s-character of the lone pair by 8% relative to **1**, which is twice as much as upon methylation of amino nitrogen in $NH_{3-m}(Me)_m$ series ($m = 0-3$). A decrease in $(IP)_n^{Koop}$ is, however, only 14.3 kcal/mol as compared to 24 kcal/mol found in going from NH_3 to NH_2Me. Apparently, sweeping generalizations based on simple concepts are not possible because each electronic structure pattern behaves differently upon substitution and protonation. In fact, eq 5 clearly shows that the protonation is not so simple as some people seem to think.

The highest s-character is found in hydrogen cyanide **7**, which leads to the highest $(IP)^{Koop}$ value being as large as 366.1 kcal/mol. Therefore, there is a high price to be paid in removing an electron from the nitrogen lone pair, which exceeds the gain in the formation of a neutral H atom (313.6 kcal/mol). However, a relatively high relaxation energy (51.3 kcal/mol) and the very strong $N(sp^1)-H$ bonding ultimately lead to the PA of 167.2 kcal/mol. Still, this is the lowest proton affinity calculated for systems scrutinized in the present work.

Perusal of results for **13** and **15** is illustrative. It is important to notice that C(1)−C(2) bond is longer than C(1)−C(3). This is indicative of the interaction between the former bond and the lone pair (vide supra). The interactions of exofunctional groups are particularly strong with the three-membered ring via Walsh, or better to say proper combinations of CC hybrid orbitals, which has important consequences in UV excitations.[39,40] The protonation of **13** increases N(1)═C(1) bond distance and makes it equivalent to those of C(2)−N(2) and C(3)−N(3), which in turn are shortened. The ring CC bond distances are substantially compressed, becoming equivalent too. These changes are reflected in rehybridization and a redistribution of π-bond orders (not shown here) in a manner compatible with a strong resonance of NH_2 groups with the ring and a strong aromatization of the three-membered ring itself. Planarization of NH_2 groups supports this contention: this is in accordance with a high relaxation energy of 64 kcal/mol (Table 1). It is important to point out that ionization from the lone pair alone produces changes in the radical cation, which are reminiscent of structural features of the conjugate acid. For example, N(1)═C(1) bond is elongated but not so much as in **13p**, whereas the bonds of the three-membered ring tend to achieve short and equal distances. They remain, however, too long and still not quite equivalent (Table 2). Similarly, the quinoid six-membered ring undergoes aromatization in the conjugate acid **15p** as evidenced by a significant stretching of N(1)═C(1) and C(6)═C(7) exo-double bonds, and there is a clear tendency of the CC bonds in the ring to become equal as much as possible. This is accompanied by shortening of $C(7)-N(sp^3)$ bond lengths and planarization of amino groups. The hybrid s-characters follow these structural changes throughout the molecule, which are triggered by rehybridization of the imino nitrogen upon the protonation with a subsequent transmission of the induced change by mobile π-electrons. Once again the ionization event induces changes in the radical cation that are characteristic of the conjugate acid, but they are less pronounced as expected.

It is important to notice that the charge of the nitrogen atom increases with the number of alkyl groups R ($R = CH_3, C_2H_5$), implying that a smaller concentration of electron density on the nitrogen atom does not automatically mean a smaller proton affinity. On the contrary, the PA increases along the series, thus illustrating once again a danger of oversimplification in attempts to reduce basicity to a single parameter. Another point of interest is the electron density placed at the new hydrogen atom attached to nitrogen in the conjugate acid. Although neither Mulliken nor Löwdin population analyses offer exact atomic charges, it is safe to say that the total electron density of H(N) in conjugate acids is close to 0.8 |e|. More specifically, the atomic charges of the proton attached to the basic nitrogen are approximately 0.34 and 0.22 |e| in the Mulliken and Löwdin descriptions, respectively, with HCN being an exception. Therefore, our tacit assumption about a full electron transfer from the base to the incoming proton is reasonable, but not exact. Moreover, since we are interested in a trend of changes of basicity within a particular series, this approximation is fully justified because the charge of H(N) is practically constant over a wider range of different, but related molecules. It is very important to realize that all qualitative conclusions would remain the same in a more realistic treatment, although the influence of the initial state would be perhaps reduced by 20−25% with an accompanying increase in the contribution of the final state.

4.3. The Solvent Effect in Acetonitrile. We have recently shown that the basicity of polyguanides in moderately polar aprotic solvent such as acetonitrile[41] could be successfully reproduced by using the isodensity polar continuum model (IPCM).[42,43] It turned out that the basicity was determined by the intrinsic gas-phase proton affinity PA_{GP} and the size of a molecule. Namely, if the positive charge is distributed over a larger number of atoms in a conjugate acid, then the polarization of the continuous solvent is smaller for an obvious reason. Consequently, the stabilization of the cation is less pronounced. Since molecules exhibiting high PAs are usually quite sizable, possessing large number of substituents, or involving several sequential fragments such as extended π-systems, the resulting basicity is given by an interplay of these two antagonistic factors. The calculation of the proton affinity of a molecule embedded in a solvent cavity requires several iterative steps. For that reason we have selected a more economical B3LYP/6-311+G**//HF/6-31G* + ZPVE(HF/6-31G*) model[41] instead of the MP2 approach using the permittivity constant for acetonitrile $\epsilon = 36.64$.

The proton affinities in acetonitrile PA(MeCN) are given in Table 3. One observes that PA(MeCN) values are much higher in solvent than in the gas phase. The point is that the conjugate acid is always more stabilized in a polar medium than the initial base. In substituted methyleneimines, chosen as a set of gauge molecules extended by some ring imine systems such as **12**−**15**, we obtained a linear relation between PA(MeCN) and PA(gas phase)

$$PA(MeCN) = 0.654 \cdot PA(5)_{GP} + 134.6 \quad kcal/mol \qquad (10)$$

which is schematically depicted in Figure 3. The quality of correlation is not very high as evidenced by inspection, which reveals appreciable scatter of points, and by the regression coefficient $R^2 = 0.94$. The average absolute error is 2.0 kcal/mol. Nevertheless, it appears that the general trend of changes is determined by the gas-phase proton affinity. It is important to notice that the gas-phase results are obtained by eq 5, which

TABLE 3: Total Molecular Energies at the B3LYP/6-311+G//HF/6-31G* Level (in shorthand notation B3LYP) in Acetonitrile**[a]

molecule	B3LYP(MeCN)	ZPVE[b]	PA(MeCN)	pK_a(theor)
1	−94.66660	24.2	270.7	14.4
1H$^+$	−95.11131	32.6		
2a	−150.06688	35.2	283.9	20.9
2aH$^+$	−150.53260	43.5		
2b	−150.06527	35.1	284.9	21.4
2bH$^+$	−150.53260	43.5		
3a	−205.45546	46.0	290.4	24.1
3aH$^+$	−205.92892	52.7		
5a	−134.00261	41.3	274.3	16.2
5aH$^+$	−134.45262	49.4		
5b	−134.00212	41.3	274.6	16.3
5bH$^+$	−134.45262	49.4		
6	−173.33528	58.1	277.5	17.7
6H$^+$	−173.79017	66.0		
7	−212.64772	74.6	279.9	18.9
7H$^+$	−213.10705	82.9		
8	−133.98657	41.1	271.4	14.7
8H$^+$	−134.43279	49.7		
9a	−173.32129	57.9	275.0	16.5
9aH$^+$	−173.77298	66.3		
9b	−173.31577	57.9	276.8	17.4
9bH$^+$	−173.77049	66.4		
10a	−189.39812	52.0	286.0	22.0
10aH$^+$	−189.86647	59.9		
10b	−189.39712	51.8	286.4	22.2
10bH$^+$	−189.86647	59.9		
12	−170.81383	30.4	283.1	20.5
12H$^+$	−171.27769	38.4		
13	−281.59251	51.7	297.8	27.8
13H$^+$	−282.07793	58.5		
14	−325.75512	73.3	282.4	20.2
14H$^+$	−326.21763	81.1		
15	−436.52913	94.3	308.6	33.1
15H$^+$	−437.03258	101.6		
NH_3	−56.58701	20.7	275.5	16.8 [16.46][c]
NH_4^+	−57.04054	29.8		
$NH_2(Me)$	−95.89702	38.5	277.9	18.0 [18.37][c]
$NH_3(Me)^+$	−96.35430	47.5		
$NH(Me)_2$	−135.21158	55.5	278.4	18.2 [18.73][c]
$NH_2(Me)_2^+$	−135.66991	64.7		
$N(Me)_3$	−174.52912	72.3	277.6	17.8 [17.6][c]
$NH(Me)_3^+$	−174.98626	81.6		

[a] The total molecular energies are given in a.u.; the proton affinity in acetonitrile and ZPVEs are given in kcal/mol. [b] ZPV energies are calculated at the HF level for free molecules being subsequently scaled by 0.89.[18] [c] Experimental pK_a(MeCN) values are taken from ref 44.

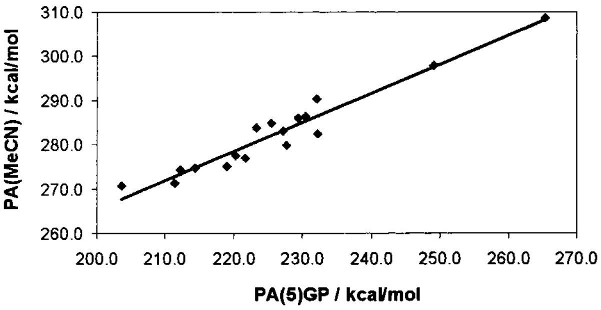

Figure 3. Linear dependence of the proton affinity in acetonitrile on the PA in the gas phase for imines obtained by eq 5.

allows for a simple interpretation of the proton affinities. Since the $PA(5)_{GP}$ values are multiplied by 0.654, it follows that all qualitative conclusions for imines **1**−**15** hold in acetonitrile, too. It should be strongly pointed out that the linear relation holds for molecules possessing a characteristic C=NH imine fragment. Although the proton affinity PA(MeCN) for guanidine estimated by eq 10 is too low by 4 kcal/mol, it is beyond doubt that its basicity in acetonitrile is determined by the gas phase proton affinity and therefore by the final state effect. It would be too presumptuous to apply eq 10 to ethylamines or HCN. For instance, the PA(actn) values for NH_3, $NH_2(Et)$, $NH(Et)_2$, and $N(Et)_3$ are 275.0 (267.4), 277.5 (275.3), 277.8 (281.9), and 278.6 (286.9), respectively, where the estimates computed by eq 10 are given within parentheses. Agreement between these two sets of data is obviously poor, thus illustrating limitations of eq 10. Moreover, pK_a(theor) for H−C≡N would be −2.8, which is clearly nonsense. This example is an eloquent *caveat emptor* that a simple approach should not be pushed too far and that its results should be handled with great care.

We have found that there is a very useful relation between PA(MeCN) and the corresponding pK_a values,[41]

$$pK_a(\text{theor}) = 0.4953 \cdot \text{PA(MeCN)} - 119.7 \qquad (11)$$

with the regression coefficient $R^2 = 0.997$ and the absolute average error as low as 0.4. The estimated pK_a(theor) values are presented in Table 3. They serve the purpose of helping the practicing chemists in assessing the measured pK_a values in their work in the future. It is eye-catching that system **15** should be a very basic compound indeed (pK_a = 33.1). In conclusion, a comment on the $NH_{3-m}(Me)_m$ series is in place. The experimental pK_a values are fortunately available,[44] which are well reproduced by our calculations (Table 3). We know that PA_{GP} steadily increases along the series being predominantly influenced by the initial state effect (Table 1). In acetonitrile the situation is somewhat different. It appears that the pK_a increases up to $NH(Me)_2$, but then a seemingly surprising descent takes place in $N(Me)_3$. It is a consequence of the solvent effect, which decreases basicity for more bulky molecules and in $N(Me)_3$, and it apparently overcomes the increase in the intrinsic (gas phase) proton affinity caused by substitution of the third methyl group. It follows as a corollary that the trend of changes in methylamines is influenced not only by the intrinsic PA, but also by solvation, which in turn exerts a dominating effect in trimethylamine.

5. Relation to Other Work and Concluding Remarks

We have shown that there is a simple and intuitively appealing picture of the protonation process, which offers a new and useful interpretive tool. It involves the following trichotomy: (1) pruning of the electron from a base in question, (2) electron capture by the incoming proton with a subsequent formation of the hydrogen atom, and (3) creation of the homolytic chemical bond between the hydrogen and radical cation. This viewpoint explains the fact that the proton affinities are much higher than the corresponding bond energies as a rule. It enables classification of neutral nitrogen bases into three categories: (a) those exhibiting the proton affinity determined by the initial state features (alkylated ammonia and alkyl derivatives of methyleneimine), (b) compounds whose basic properties are dictated by the final state effects occurring in conjugate acids (amine derivatives of methyleneimine and polyguanides), and (c) systems where both initial and final state effects are strongly interlocked such as, for example, in phosphazenes. In molecules belonging to groups (b) and (c), the relaxation energy plays a very important role. Since an electron is never completely shifted to the proton, it follows that the proposed picture represents an idealization of a true process. However, it is important to realize that a more realistic approach would probably diminish the contributions of the initial state by 20−25%, but would not change the general qualitative conclusions. The final expression is, however, exact and the only approximations involved are those introduced by computations. Although we presented a considerable amount of numerical data, the emphasis in this work was on the conceptual side of the problem. It has been shown that the protonation and the accompanying proton affinity can be reduced to very few terms embodied in eq 5, which enable a deeper holistic understanding of the process. It is, however, of the utmost importance to be aware of the fact that understanding of the guiding principles of a phenomenon under scrutiny always has some interesting practical consequence. For instance, the unexpected finding that a very low $(\mathrm{IP})_1^{\mathrm{Koop}}$ value leads to high proton affinity of 1,1-diaminoethylene **11** enables a straightforward generalization. Our preliminary calculations show that polyenes substituted by CH_3 and NH_2 groups at suitable positions represent surprisingly strong carbon bases.[45] We are confident that the concepts developed here will be useful in tailoring powerful neutral organic superbases.

It is of some interest to compare the present picture of protonation with that introduced by Shirley et al.[46,47] some twenty years ago. In their completely different approach the proton is bound to the basic atom in two steps. The first involves attachment of the proton without any charge transfer and without any electron density polarization. Consequently, the first step corresponds to Koopmans' frozen molecule approximation. Since a placement of the proton in the close vicinity of the nucleus of the basic atom is (almost) equivalent to ionization of its inner shell, the corresponding energy is equal to $-\epsilon_{1s}(\mathrm{N})$, where ϵ_{1s} stands for the 1s MO energy and N denotes the nitrogen atom to be protonated. In the second step, the electron density drift is permitted, which is accompanied with the electron density relaxation effect yielding a stabilization of the conjugate acid denoted by $E(\mathrm{N})_{\mathrm{relax}}$. The proton affinity is given then by eq 12

$$\mathrm{PA} = -\epsilon_{1s}(\mathrm{N}) - E(\mathrm{N})_{\mathrm{relax}} \qquad (12)$$

where $E(\mathrm{N})_{\mathrm{relax}}$ is defined as a positive entity.[48] Hence, in Shirley's approach, Koopmans' inner-core orbital energy reflects properties of the initial base, whereas $E(\mathrm{N})_{\mathrm{relax}}$ gives a contribution of the final state to the resulting proton affinity. Shirley et al. found eq 12 useful in discussing the basicity of alkyl derivatives of simple alcohols and in establishing a relation between PAs and ESCA shifts in amines and phosphines.[46,47] It should be recalled that if the PAs are correlated with experimental ESCA shifts, then some influence of the relaxation effect is implicitly incorporated since the latter are affected by the final state reorganization energy.[48] In an interesting study of azoles, Mó et al.[49,50] found that their proton affinities could be successfully correlated with $-\epsilon_{1s}(\mathrm{N})$ and HOMOs of neutral bases via multivariate linear analysis,

$$\mathrm{PA} = f(-\epsilon_{1s}(\mathrm{N}), E(\mathrm{HOMO}))_{\mathrm{ML}} \qquad (13)$$

where the index ML denotes a multilinear relation. It appeared that the proton affinities of azoles were determined by their electronic features in the initial state. Obviously, this formula can be applied only to a series of closely related compounds exhibiting pronounced initial state effects, provided the final state contributions remain reasonably constant. Both eqs 12 and 13 differ from our trichotomy picture embodied in eq 5 in one very important aspect: they are approximate in nature. As it was pointed out earlier, eq 5 was somewhat arbitrary, but it was nevertheless both legitimate and exact in principle. The latter follows from the fact that exact proton affinities are obtained if all three terms appearing in eq 5 are calculated with a sufficient accuracy. In contrast, eqs 12 and 13 are semiempirical from the outset, implying that the range of their applications is limited to families of intimately related molecules only.

Finally, a word on hardness of neutral bases is in place here. Briefly, Parr and Pearson[51] defined molecular hardness as the quantity η,

$$\eta = (1/2)(\mathrm{IP} - \mathrm{EA})\eta \cong (1/2)(\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}) \qquad (14)$$

where IP and EA denote the first ionization potential and electron affinity, respectively. Again, eq 14 can provide some description of the initial state effect of the protonation process, but it falls short in retrieving the influence of the final state.

It should be mentioned at the very end that a useful byproduct of the present study is given by the adiabatic potentials, which in turn are in good agreement with available experimental data. Finally, the solvent effect in acetonitrile is examined and it is shown that the proton affinities of imines in this moderately polar aprotic solvent follow the gas phase values to a fairly high degree. In contrast, the solvent effect in methylamines is very important and has to be explicitly taken into account, if a correct hierarchy of basicity is desired.

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