J. Am. Chem. Soc. 1980, 102, 5222-5226

Determination of Circumstances under Which the Correlation of Core Binding Energy and Gas-Phase Basicity or Proton Affinity Breaks Down

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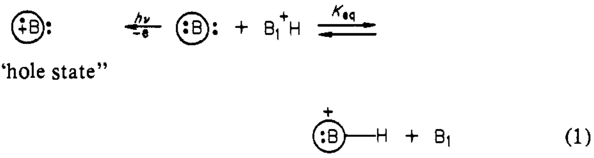
Abstract: Correlations between E_B and gas-phase $\Delta G°$ or PA values are valid only if the site of protonation and ionization are the same and if large geometry changes do not accompany protonation. $N_{1s}E_B$ and $\Delta G°$ values for various amides do not fit the correlation given for other amines because the amides are probably oxygen protonated in the gas phase. However, amide $O_{1s}E_B$ and $\Delta G°$ values correlate well. Several compounds are presented which undoubtedly are nitrogen protonated but do not fit the expected correlation presumably because upon protonation, there are substantial geometry changes occurring. One can use the deviation from the line for these points to estimate the energy associated with the geometric changes.

I. Introduction

In the past few years many studies have been reported correlating core binding energies $E_{\mathrm{B}1s}$ with gas-phase proton affinities (PA) or basicities ($\Delta G°$, defined as in eq 1) for diverse species



N_{1s} "hole state"

(1)

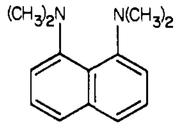
$$\Delta G° = -RT \ln K_{eq}$$
$$\mathrm{PA} = -\Delta H° \text{ (relative to the standard PA for } B_1\text{)}$$

containing nitrogen, oxygen, phosphorus, arsenic, and sulfur.[1] Some theoretical work supporting the E_B vs. PA correlations has been reported,[1b,c,2] and correlations have also been reported between first ionization potentials (IP's) and PA.[1c,3] The photoionization process is a vertical one in the Franck–Condon sense, requiring that the geometries of the ground and ion states remain the same. Hence factors influencing the photoemission process relate to electronic (inductive and mesomeric) effects in the ground and ion states. On the other hand, gas-phase basicity values may be considered adiabatic in the sense that the protonated species are fully relaxed electronically as well as geometrically as is required by the equilibrium conditions.

The main assumptions under which correlations between $E_{\mathrm{B}1s}$ and $\Delta G°$ (or $\Delta H°$) will hold are (a) that the site of protonation and ionization are the same and (b) that within a series of closely related bases there are not large energetically different geometry changes accompanying protonation.[4] These fundamental assumptions have been often noted[1,3] but have been specifically invoked in only a few cases.[1a,d,e,g] In order to further probe these questions, we set out to experimentally investigate molecules which should deviate from the correlation for one or both of the above reasons.

Amides represent a class of compounds for which oxygen protonation is observed for both solution and solid phases[5] and some theoretical analysis has been reported.[6] Thus the correlation of $N_{1s}E_B$ and $\Delta G°$ should break down but that for $O_{1s}E_B$ should hold.[1e] Earlier work from these laboratories[1g] showed that the $N_{1s}E_B$ value for 2-pyridone could not possibly correlate with its basicity, and we now extend this study to include all amides for which gas-phase $\Delta G°$ values are reported.

To our knowledge there has been but one study[1d] which demonstrated that favorable geometry changes normally accompanying protonation were inhibited by the substrate structure, leading to a lack of correlation between E_B and PA. Relatively few molecules have been studied by any technique for which unusually favorable geometry changes occur on protonation. However, one of these, the so-called "proton sponge" (I), has been investigated in considerable detail in order to explain its unusally high basicity in both gas[7a] and solution phases.[7b,c] Crystallographic data for I[7e]



I

indicate that the bis(dimethylamino) groups experience severe peri interaction causing a large distortion from planarity for the naphthalene ring. Protonation of I gives its conjugate acid a

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(1) (a) Mills, B. E.; Martin, R. L.; Shirley, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 2380–2385 (oxygen, nitrogen, phosphorus, sulfur). (b) Martin, R. L.; Shirley, D. A. *Ibid.* **1974**, *96*, 5299–5304 (oxygen, nitrogen). (c) Davis, D. W.; Rabalais, J. W. *Ibid.* **1974**, *96*, 5305–5310 (oxygen, nitrogen). (d) Ashe, A. J.; Bahl, M. K.; Bomben, K. D.; Chan, W.-T.; Gimzewski, J. K.; Sitton, P. G.; Thomas, T. D. *Ibid.* **1979**, *101*, 1764–1797 (phosphorus, arsenic). (e) Cavell, R. G.; Allison, D. A. *Ibid.* **1977**, *99*, 4203 (nitrogen). (f) Benoit, F. M.; Harrison, A. G. *Ibid.* **1977**, *99*, 3980–3984 (singly and doubly bonded oxygen). (g) Brown, R. S.; Tse, A.; Vederas, J. C. *Ibid.* **1980**, *102*, 1174–1176. (h) Brown, R. S.; Tse, A. *Can. J. Chem.*, in press (pyridines). (i) Carroll, T. X.; Smith, S. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1975**, *97*, 659–660. (j) Smith, S. R.; Thomas, T. D. *Ibid.* **1978**, *100*, 5459–5466.

(2) Catalãn, J.; Mō, O.; Pērez, P.; Yãñez, M. *J. Am. Chem. Soc.* **1979**, *101*, 6520–6524 and references therein.

(3) (a) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4136–4137. (b) Yoshikawa, K.; Hashimoto, M.; Morishima, J. *Ibid.* **1974**, *96*, 288–289. (c) DeKock, R. L.; Barbachyn, M. R. *Ibid.* **1979**, *101*, 6516–6519. (d) Zverev, V. V. *Zh. Obshch. Khim.* **1978**, *48*, 2171–2174; *J. Gen. Chem. USSR* (*Engl. Transl.*) **1978**, *48*, 1973–1976.

(4) Geometric changes must accompany all protonations, but the correlation can be expected only if regular reorganization energies are involved for each base within a series.

(5) (a) Gillespie, R. J.; Birchall, T. *Can. J. Chem.* **1963**, *41*, 148–155. (b) Moehrle, H. et al. *Monatsh. Chem.* **1978**, *109*, 1295–1303. (c) Sarneski, J. E.; Surprenant, H. L.; Reilley, C. N. *Spectrosc. Lett.* **1976**, *9*, 885–894. (d) Diop, L.; Belin, C.; Potier, *J. Chim. Phys.-Chim. Biol.* **1976**, *73*, 207–212. (e) Stilbs, P.; Forsen, S.; Hartman, J. S. *J. Chem. Soc., Perkin Trans. 2* **1977**, 556–558. (f) Kabanor, V. P.; Khar'kov, S. N. *Zh. Prikl. Khim.* (*Leningrad*) **1975**, *48*, 2703–2707; *J. Appl. Chem.* USSR (*Engl. Transl.*) **1975**, *48*, 2784–2786 and earlier references therein.

(6) (a) Hinton, J. F.; Beeler, A.; Harpool, D.; Briggs, R. W.; Pullman, A. *Chem. Phys. Lett.* **1977**, *47*, 411–415 (ab initio-SCF calculations on Li^+ affinity of amides). (b) Kollman, P.; Rothenberg, S. *J. Am. Chem Soc.* **1977**, *99*, 1333–1342.

(7) (a) Lau, Y. K.; Saluja, P. P. S.; Kebarle, P.; Alder, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 7328–7333. (b) Hibbert, F. *J. Chem. Soc., Chem. Commun.* **1973**, 463. (c) Alder, R. W.; Bowman, P. S.; Steele, W. R. S.; Winterman, D. R. *Ibid.* **1968**, 723–724. (d) Alder, R. W.; Anderson, J. E *J. Chem. Soc., Perkin Trans. 2* **1973**, 2086–2088. (e) Einspahr, H.; Robert, J.-B.; Marsh, R. E.; Roberts, J. D. *Acta Crystallogr., Sect. B* **1973**, *29*, 1611–1618. (f) Truter, M. R.; Vickery, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 395–403.

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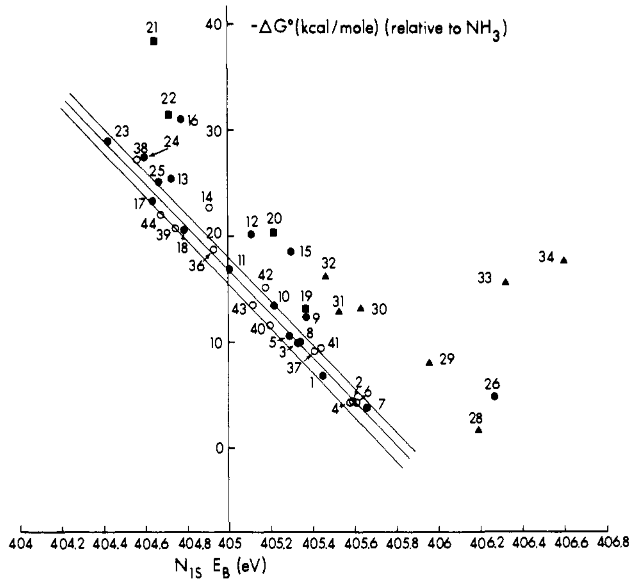

Figure 1. A plot of the $N_{1s}E_B$ values against reported $-\Delta G°$ values (relative to ammonia) for the compounds listed in Table I. Amides are represented as closed triangles, pyridines as open circles, anilines as closed circles, and naphthylamines as closed squares. For explanation of the triple line, see text.

structure[7f] in which the bis(dimethylamino) groups are reoriented to share the proton between them with concomitant flattening of the ring, albeit not to complete planarity.[7f] Thus part of the basicity of I must be ascribed to a relief of ground-state strain on protonation, a process which cannot be probed by the photoemission process. The following report demonstrates the expected lack of correlation between $N_{1s}E_B$ and $\Delta G°$ values for such compounds and futhermore allows one an indirect experimental measurement of the energy associated with such geometric changes.

II. Results

Nitrogen and oxygen $E_{B_{1s}}$ values and existing gas-phase basicities for several compounds are presented in Table I. E_B values are the average of at least three consecutive determinations and are calibrated against an internal standard neon Auger line of KE = 804.56 eV.[8] $\Delta G°$ values were abstracted from published work of Kebarle,[7a] Taft,[9] and Aue,[10] the latter two sets of data being determined by ICR experiments at 300 K, and the former by high-pressure mass spectrometry at 600 K but are corrected to 300 K.[11]

A plot of the $N_{1s}E_B$ values against $\Delta G°$ for all compounds including pyridines **36–44**[1h] is shown in Figure 1, and it can be seen that a substantial number of examples deviate from the enclosed line. The triple "line" is the correlation for a number of model compounds for which (a) the site of protonation is undoubtedly nitrogen, i.e., pyridines,[1g,h] quinuclidine (**23**), Dabco (**25**), and some anilines (vide infra) and (b) geometry changes accompanying protonation are small since the rigid structures should oppose large geometry changes. The width represents a rather generous ±1 kcal/mol error limit for the E_B or $\Delta G°$ values, and the best fit straight line encompassing 21 bases within the width is $\Delta G° = 20.6486(N_{1s}E_B) - 8379.37$ kcal/mol; $r = 0.994$. The examples which lie considerably off this line are those to which discussion will be limited.

Table I. $E_{B_{1s}}$ and $\Delta G°$ Values Relative to NH_3[a]

	compd	$N_{1s}E_B$, eV	$\Delta G°$, kcal/mol
1	aniline	405.45	-6.7^b
2	*p*-fluoroaniline	405.59	-4.59^c
3	*p*-methylaniline	405.33	-10.1^c
4	*p*-chloroaniline	405.58	-5.1^c
5	*p*-methoxyaniline	405.29	-10.9^d
6	*m*-fluoroaniline	405.61	-3.5^c
7	*m*-chloroaniline	405.66	$-3.6,^c -2.8^b$
8	*m*-methylaniline	405.34	-10.1^c
9	*m*-methoxyaniline	405.37	-12.4^d
10	*N*-methylaniline	405.22	-13.5^b
11	*N*-ethylaniline	405.01	-16.9^b
12	*N*,*N*-dimethylaniline	405.11	$-20.1,^b -19.8^c$
13	*N*,*N*-diethylaniline	404.73	-25.4^b
14	*N*-methyl-*N*-ethylaniline	404.91	-22.7^b
15	*m*-aminoaniline	405.30	-18.5^b
16	*o*-bis(dimethylamino)benzene	404.78	-31.0^b
17	*N*-phenylpiperidine	404.64	-23.3^c
18	*N*-phenylpyrrolidine	404.79	-20.6^c
19	1-aminonaphthalene	405.37	-13.1^b
20	1,8-diaminonaphthalene	405.22	-20.3^b
21	1,8-bis(dimethylamino)-naphthalene	404.65	-38.4^b
22	1-(*N*,*N*-dimethylamino)-8-(*N*-methylamino)naphthalene	404.72 ± 0.04	-31.4^b
23	quinuclidine	404.43	-28.9^c
24	benzoquinuclidine	404.61	-27.7^c
25	1,4-diazabicyclooctane	404.67	-25.1^c
26	pyrrole	406.27	-4.8^b

Amides

	compd	$N_{1s}E_B$, eV	$O_{1s}E_B$, eV	$\Delta G°$, kcal/mol
27	formamide	406.45	537.96	
28	*N*-methylformamide	406.19	537.48	-1.8^c
29	*N*,*N*-dimethylformamide	405.96	537.09	-8.1^c
30	*N*,*N*-dimethylacetamide	405.63	536.78	-13.2^c
31	*N*-methylpyrrolidone	405.53	536.79	-13.0^e
32	*N*-methylpiperidone	405.47	536.60	-16.2^e
33	*N*-methyl-2-pyridone[f]	406.33	536.36	-15.5^e
34	2-pyridone[f]	406.61	536.66	*g*
35	*N*,*N*-diethylacetamide	405.33	536.59	

Pyridines

	compd	$N_{1s}E_B$,[h] eV	$\Delta G°$,[c] kcal/mol
36	pyridine	404.94	−17.7
37	3-(trifluoromethyl)pyridine	405.41	−9.1
38	3-(dimethylamino)pyridine	404.57	−27.2
39	3-methylpyridine	404.75	−20.6
40	3-chloropyridine	405.20	−11.5
41	4-(trifluoromethyl)pyridine	405.44	−9.4
42	4-bromopyridine	405.18	−15.2
43	4-fluoropyridine	405.12	−13.5
44	4-methylpyridine	404.68	−22

[a] $E_{B_{1s}}$ precision ±0.03 eV unless otherwise noted. $\Delta G°$ values[7a] corrected to 300 K and are relative to NH_3. [b] Reference 7a. [c] Reference 9. [d] Reference 14. [e] Reference 10. [f] Reference 1g. [g] No $\Delta G°$ value reported but estimated to be close to that of pyridine.[1g] [h] Reference 1h.

III. Discussion

(i) **Amides (27–34).** In Figure 1, amides are represented by closed triangles and in general are located well above the line; they are more basic than the $N_{1s}E_B$ values would suggest. For the simple amides (**28–32**) a line roughly parallel to but about 6–8 kcal/mol above the line for the other nitrogen bases is observed ($\Delta G° = 17.425(N_{1s}E_B \text{ amide}) - 7080.63$ kcal/mol; $r = 0.980$). Oddly enough, an experimental basicity for formamide (**27**) has not been reported, although a PA of 194 kcal/mol (relative to a PA of 207 kcal/mol for NH_3) was given in a theoretical study.[6b] If we insert the $N_{1s}E_B$ for formamide into the above equation (for

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(8) Thomas, T. D.; Shaw, R. W. *J. Electron Spectrosc.* **1974**, *5*, 1081–1094.

(9) (a) Taft, R. W. In "Proton Transfer Reactions"; Calden, E., Gold, V., Eds.; Chapman and Hall: London, 1975; p 31. (b) We thank Professor Taft for informing us about corrected $\Delta G°$ values. (c) Kebarle, P. *Ann. Rev. Phys. Chem.* **1977**, *28*, 445–476.

(10) (a) Aue, D. H.; Betowski, L. D.; Davidson, W. R.; Bowers, M. T.; Beak, P.; Lee, J. *J. Am. Chem. Soc.* **1979**, *101*, 1361–1368. (b) We thank Professor Aue for providing us with certain pyridine basicities.

(11) Corrected according to $\Delta G°_{300} = (\Delta G°_{600} + \Delta H°)/2$. We thank Dr. Y. K. Lau for providing us with the $\Delta H°$ values for compounds in ref 7a.

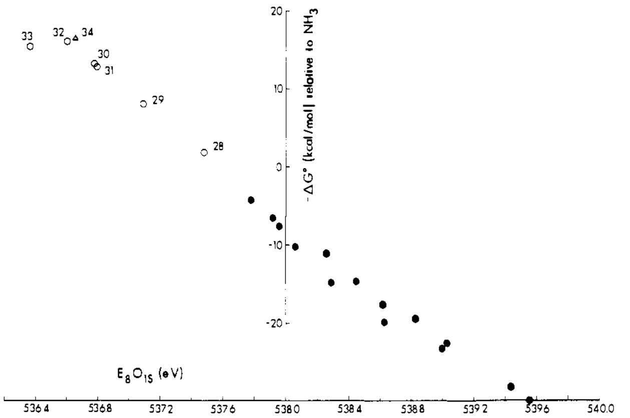
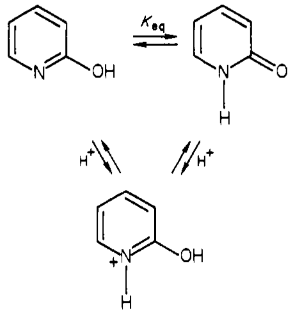


Figure 2. A plot of $O_{1s}E_B$ against $-\Delta G°$ (relative to ammonia) for carbonyl oxygen-containing species. The open circles are for amide data from this work, while the closed circles are transcribed from $O_{1s}E_B$ data in ref 1j. The open triangle is a predicted basicity for 2-pyridone from ref 1g.

amides) a basicity of about 1.8 kcal/mol less than that of NH_3 is predicted. This is qualified, however, by the observation that amides **33** and **34** appear to deviate markedly from the limited correlation given for the simple amides.

Our earlier work[19] on the 2-hydroxypyridine ⇄ 2-pyridone equilibrium (eq 2) showed a gas phase $K_{eq} \simeq 0.5$ at 130 °C, leading to a free-energy difference between the tautomers of $\Delta G_2° = 0.58 \pm 0.08$ kcal/mol, confirming existing experimental results.[10a,12a] At 240 °C we find virtually no change in the integrated N_{1s} or O_{1s} ratios for the tautomers (i.e., $K_{eq}(240\ °C) = 0.51 \pm 0.02$) from those found at 130 °C. From the van't Hoff equation[12b] this leads to an experimental enthalpy difference between the two forms of $\Delta H°_2 = 0.23 \pm 0.55$ kcal/mol, in excellent agreement with Beak's value of $\Delta H° = -0.3 \pm 0.3$ found from gas-phase UV studies.[12a]

From the thermodynamic cycle in eq 2, the gas-phase basicity



(2)

$$K_{eq} \simeq 0.5$$
$$\Delta G_2° = -RT \ln K_{eq}$$

of the pyridine and pyridone forms cannot differ by more than 0.58 kcal/mol, even though the former is N protonated while the latter is O protonated. That the $N_{1s}E_B$ for 2-pyridone is 1.65 eV greater than that for 2-hydroxypyridine (406.61 vs. 404.96 eV) even though the basicities cannot be appreciably different provides unquestionable evidence for the lack of correlation between E_B and $\Delta G°$ when the sites of protonation and ionization are different. As stated above, *N*-methyl-2-pyridone (**33**) does not fit the limited correlation seen for the simpler amides but is far more basic than expected on the basis of its N_{1s} ionization energy. This must certainly be due to the fact that on O protonation, **33** will relax electronically to a charged aromatic species whereas no equivalent electronic relaxation can accompany the N_{1s} photoionization. A similar observation is made for 2-pyridone (**34**) although the basicity is not an experimental value but a predicted one.[1g] Pyrrole (**26**) also falls well above the line in Figure 1 which supports ring but not nitrogen protonation.[1e,13] Since available evidence[5,6] favors O protonation for amides, one might expect that a plot of $O_{1s}E_B$ vs. $\Delta G°$ would show a considerably better fit than that given in Figure 1. Shown in Figure 2 is such a plot utilizing available gas-phase basicity data[9a,c] for some acids, esters, ketones, and aldehydes (closed circles; $O_{1s}E_B$ data from ref 1j) as well as the amides reported in this work. The correlation for the former carbonyl-containing species has already been presented by Smith and Thomas[1j] and in part by Benoit and Harrison,[1f] although it has been noted[1j] that the latter's correlation[1f] represents the carbonyl data rather poorly. It is clear however from Figure 2 that the amides (open circles) from this work fit the correlation remarkably well, the best-fit straight line being $\Delta G° = 16.352(O_{1s}E_B) - 8791.28$ kcal/mol ($r = 0.9948$ for 20 data). This observation provides convincing evidence that the amides, like esters, ketones, and aldehydes, are C=O protonated and their basicity can be accurately probed by considering the O_{1s} ionization energy. Although the basicity value for **34** is predicted, one sees that the pyridones **33** and **34** fit the line well, lending support to the idea that electronic relaxation accompanying O_{1s} photoemission is similar to that accompanying oxygen protonation. From the best fit line in Figure 2, formamide (**27**) is predicted to have a basicity 5.4 kcal/mol less than ammonia. We feel the quality of the fit allows a greater degree of confidence in this basicity than that predicted on the basis of the $N_{1s}E_B$.

(ii) Substituted Anilines (1–19). Much attention has been given to the gas-phase basicities of aniline derivatives, particularly with an eye to determining the site of protonation.[1e,7a,14] Recent theoretical work[14] has favored N protonation for aniline (**1**) and *N*,*N*-dimethylaniline (**12**). From Figure 1, one sees that the data for the anilines (**1–8, 10, 11, 17–18**) lie on the line which suggests that these molecules are nitrogen protonated in agreement with predictions.[14] Anilines **9** and **15** (*m*-OCH_3 and *m*-NH_2, respectively) deviate upwards from the line as expected if these materials protonate on the ring preferentially,[14] and we will report further on this question in the future.[15]

Aniline (**1**) has been demonstrated to be nonplanar in the gas phase by microwave,[16a] UV,[16b] and far-infrared studies[16c–e] with some theoretical verification.[16f] The angle between the plane of the ring and the H–N–H plane (θ in II) has been determined to be between 42[16d,e] and 46°.[16b] Solution phase data for substituted anilines indicate θ is large for electron donors and smaller for electron withdrawers, being near 0° for *p*-nitroaniline.[17] In the gas phase, however, θ for *p*-fluoroaniline is reported to be 46.4[18] and 43°.[16c] *N*-Methylaniline (**10**) (and presumably *N*-ethylaniline (**11**)) is also nonplanar, the value of θ being estimated at 38.5° from dipole moments.[19]

On the other hand, *N*,*N*-dimethylaniline (**12**) appears to be somewhat more planar, with θ being less than 20° in solution[20] (earlier determinations were somewhat greater[19]). Vapor-phase electron diffraction measurements for **12** indicate little deviation from planarity for the system[21] (θ is small).

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[12] (a) Beak, P. *Acc. Chem. Res.* **1977**, *10*, 186–192 and references therein. (b) $\ln (K_{eq(T_2)}/K_{eq(T_1)}) = -(\Delta H°/R)(1/T_2 - 1/T_1)$; Nash, L. K. "Elements of Chemical Thermodynamics", 2nd ed.; Addison-Wesley: Reading, Mass., 1970; p 134.

[13] Chiang, Y.; Whipple, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 2763–2767.

[14] (a) Pollack, S. K.; Delvin, J. L., III; Summerhays, K. D.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4483–4485. (b) Summerhays, K. D.; Pollack, S. K.; Taft, R. W.; Hehre, W. J. *Ibid.* **1977**, *99*, 4485–4487 and references therein.

[15] Brown, R. S.; Kebarle, P.; Tse, A.; Nishizawa, K., full results to be submitted for publication.

[16] (a) Lister, D. G.; Tyler, J. K. *J. Chem. Soc., Chem. Commun.* **1966**, 152–153. (b) Brand, J. C. D.; Williams, D. R.; Cook, T. J. *J. Mol. Spectrosc.* **1966**, *20*, 359–380 (θ = 46°). (c) Kydd, R. A.; Krueger, P. J. *Chem. Phys. Lett.* **1977**, *49*, 539–543. (d) Qwack, M.; Stockberger, M. *J. Mol. Spectrosc.* **1972**, *43*, 87–116 (θ = 42°). (e) Larsen, N. W.; Hansen, E. L.; Nicolaisen, F. M. *Chem. Phys. Lett.* **1976**, *43*, 584–586 (θ = 42°). (f) Stramitz, C. C.; Schmidtke, H.-H. *Theor. Chim. Acta* **1976**, *42*, 13–22.

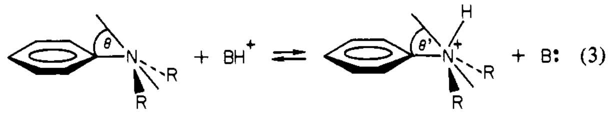
[17] (a) Cumper, C. W. N.; Singleton, A. *J. Chem. Soc.* **1967**, 1096–1100, 1100–1103. (b) Aroney, M. J.; Calderbank, K. E.; LeFèvre, R. J. W.; Pierens, R. K. *Ibid.* **1968**, 561–565.

[18] Hastie, A.; Lister, D. G.; McNeil, R. L.; Tyler, J. K. *J. Chem. Soc., Chem. Commun.* **1970**, 108–109.

[19] Smith, J. W. *J. Chem. Soc.* **1961**, 81–86.

[20] Aroney, M. J.; LeFèvre, R. J. W.; Radom, L.; Ritchie, C. L. D. *J. Chem. Soc.* **1968**, 507–512.

N protonation of an aniline derivative (eq 3) must yield an



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anilinium ion having close to tetrahedral geometry ($\theta' = 54.7°$) at nitrogen. Thus if the starting aniline is close to planarity (θ is small) a significant geometry change (rehybridization) must accompany protonation, its magnitude progressively diminishing as θ becomes larger. For aniline and *p*-fluoroaniline which have large values of θ, one does not expect extensive rehybridization upon protonation. While little structural information is available for *N*-phenylpiperidine (**17**) and *N*-phenylpyrrolidine (**18**), molecular models indicate the saturated ring should hold the nitrogen approximately tetrahedral so large geometry changes should not be expected on protonation. From Figure 1, compounds **1**–**8**, as well as **10**, **11**, **17**, and **18**, fall within the constraints of the correlation, supporting the idea that large geometry changes on protonation are not occurring. However, **12**, **13**, and **14**—the *N*,*N*-dialkylanilines—fall substantially above the line consistent with expectations concerning a protonation–rehybridization for these which cannot be probed by E_B determinations.

An earlier correlation of E_B vs. PA for various amines[1e] considered the deviation of *N*,*N*-dimethylaniline from the correlation to arise either from "stabilization of its ground state or destabilization of the N_{1s} hole state" relative to those for aniline or *N*-methylaniline.[22] Our present results indicate that the deviation of **12** in Figure 1 is better explained on the basis of geometry changes accompanying protonation. One might further use Figure 1 to estimate the energetic magnitude of such reorganization as being proportional to the vertical deviation (ca. 5 kcal/mol for **12**) from the line. Thus from vertical E_B measurements, one can account for about 15 kcal/mol of the basicity of **12** (relative to NH_3) on the basis of electronic effects and a further 5 kcal/mol on the basis of geometric reorganization.

(iii) **Aminonaphthalene Derivatives (19–22).** Each of **19**–**22** lies considerably above the line in Figure 1, with the most severe deviation being that of the "proton sponge", **21**. 1-Aminonaphthalene (**19**) is suggested to prefer ring over N protonation by about 3 kcal/mol.[7a] If this were the case, it should be more basic than expected on the basis of its N_{1s} ionization energy. That **19** lies 3.4 kcal/mol above the line in Figure 1 quantitatively supports the suggestion of ring protonation,[7a] although one cannot absolutely exclude the possibility that the deviation is due to a rehybridization accompanying protonation on nitrogen. Kebarle et al.[7a] suggested that **20**–**22** (as well as *o*-bis(dimethylamino)benzene (**16**)) are N protonated with further stabilization resulting from H bonding of the proton to the second nitrogen. X-ray crystallographic data on **21**[7e] (and its conjugate acid[7f]) verify this analysis in the solid phase and furthermore indicate that the distortion from planarity of the naphthalene ring of **21**[7e] is somewhat relieved upon protonation,[7f] the two nitrogens contracting from 2.79 to 2.65 Å apart. This relief of ground-state strain is an important component of the remarkable basicity of **21**, and if vertical deviation from the line (Figure 1) can be used as a measure of steric relief on protonation, its magnitude is about 15 kcal/mol. The strain relief diminishes as methyl groups are removed from the nitrogen, the deviation being 9 and 8 kcal/mol for **22** and **20**, respectively. The 11 kcal/mol deviation of **16** can similarly be explained on the basis of N lone-pair reorientation to chelate the proton.

Table II. MINDO/3 Calculated Heats of Formation for Some Bases

	ΔH_f, kcal/mol				
	B:	$\xrightarrow{H^+}$	B:H⁺	$\longrightarrow$	BH⁺
base	base	$\Delta\Delta H_f$	vertical ion	$\Delta\Delta H_f$	adiabatic ion
pyridine (**36**)	34.1	135.3	169.4	−2.3	167.1
quinuclidine (**23**)	22.9	142.9	165.8	−2.3	163.5
4-methoxypyridine[a]	−15.8	131.4	115.6	−4.2	111.4
3-methoxypyridine[a]	−13.36	139.96	120.6	−2.5	118.10
o-diaminobenzene	12.6	148.7	161.3	−2.2	159.1[b]
				−8.4	152.9[c]
aniline[d] (1)	17.9	182.8	200.7	−35.1	165.6

[a] Reference 1h. [b] H-bonded and N lone-pairs ⊥ to benzene π system (see text). [c] Non-H-bonded (see text) with remaining N lone pair conjugated with benzene π system. [d] Calculated geometry of aniline nearly planar, contrasting with experimental data of ref 16.

(iv) **Calculations.** MINDO/3 calculations have been found to give reasonable heats of formation (ΔH_f) for a wide variety of compounds[24] and have been used to provide some insight into dihydropyridine protonations.[24b] Earlier work from our laboratories[1h] utilized the method to probe the energetic advantage of geometric reorganization in pyridine protonation. According to eq 4, protonation of a geometry optimized base B: gives a hypothetical vertical ion B:H⁺ having the same geometry as the base. Geometry optimization of the vertical ion gives an adiabatic ion with concomitant release of heat.

$$\mathrm{B}: \overset{\mathrm{H}^+}{\rightleftharpoons} \underset{\text{vertical ion}}{[\mathrm{B{:}H}]^+} \rightleftharpoons \underset{\text{adiabatic ion}}{\mathrm{B{-}H}^+} \qquad (4)$$

If the molecular structure opposes such geometry changes, the difference between the calculated adiabatic and vertical ions should be small. On the other hand, if geometry changes are large (for example sp^2–sp^3), then the calculated differences in ΔH_f for the two ions should reflect this by giving a large stabilization for the adiabatic ion.

Table II lists the results for typical bases such as pyridine (**36**) or quinuclidine (**23**) which are not expected to undergo large geometry changes, and it can be seen that the calculated differences between adiabatic and vertical ions are both −2.3 kcal/mol. Of course for those compounds which define the "line" given in Figure 1, this small energy gain due to rehybridization accompanying protonation is incorporated into the correlation by an alteration of the $-\Delta G°$ intercept upwards by ~2–3 kcal/mol. One must be aware, however, that not all "rigid" nitrogen bases will have the same vertical → adiabatic ion heat release. For example, from Table II, one sees that the calculated vertical → adiabatic $\Delta\Delta H_f$ for 4-methoxypyridine is −4.2 kcal/mol while that for 3-methoxypyridine is −2.5 kcal/mol. Therefore even for rigid bases, some slight discrepancy in the line should be expected and is found (e.g., **38**, **41**, and **42**). Shirley et al.[1a] have noted that each of a series of primary, secondary, and tertiary amines have the same slope but a different intercept, supporting the idea that the geometric changes within any one series are energetically similar but are of different magnitude from the next series.

While the calculated ΔH_f for **1** in Table II is the same as that reported,[24a] the calculation fails to reproduce the experimental geometry[16] and prefers to hold the amino group nearly planar (sp^2)

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(21) Vilkov, L. V.; Timasheva, T. P. *Dokl. Akad. Nauk SSSR* **1965**, *161*. 351–354; *Dokl. Chem.* (*Engl. Transl.*) **1965**, *161*, 261–264.

(22) If this were so, one might expect that **12** should show an unexpectedly high $N_{1s}E_B$ and an irregular methyl-substitution effect in passing from aniline (**1**) to *N*-methylaniline (**10**) to *N*,*N*-dimethylaniline (**12**) would be observed. Successive methylation of **1** (Table I) shifts the E_B by 0.23 and 0.11 eV. Reported E_B values for methyl- (405.14 eV),[23] dimethyl- (404.90 eV),[23] and trimethylamine (404.79 eV)[23] indicate substitution effects identical with those found for the anilines and hence no unusual stabilization or destabilization of the ground or ion states for **12**.

(23) Finn, P.; Pearson, R. K.; Hollander, J. M.; Jolly, W. L. *Inorg. Chem.* **1971**, *10*, 378–381.

(24) (a) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285–1318. (b) Bodor, N.; Pearlman, R. *Ibid.* **1978**, *100*, 4946–4953. (c) It has been pointed out that in its present parameterization, the MINDO/3 method fails to yield for the experimental geometry for some simple substituted amines and is probably not a reliable method for producing a complete and reliable structural theory.[24d] (d) Hehre, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 5308–5310.

and conjugated with the ring.[24c,d] Nevertheless since N protonation of **1** should give an anilinium ion with a pseudotetrahedral (sp^3) N, this case should indicate the magnitude of the rehybridizational energy associated in passing from an sp^2 neutral to an sp^3 ion. Since the vertical ion is a hypothetical entity, no significance should be attached to its calculated ΔH_f, other than as a reference number with which to compare ΔH_f for the adiabatic ion. The calculated difference is large (−35.1 kcal/mol), supporting the idea that correlations between vertical and adiabatic process will break down if the latter involves substantial geometry changes.

As a model for **16**, the same approach was attempted for *o*-diaminobenzene in the hope of calculating a preferred H-bonded structure for its ion. The calculated value of 159.1 kcal/mol refers to the H-bonded structure in which the proton is asymmetrically bound between the two N lone pairs which are twisted orthogonal to the ring π system but does not represent an energy minimum. Full geometry optimization for the H-bonded species finally minimizes (ΔH_f = 152.9 kcal/mol) in a non-H-bonded geometry in which both amino groups have been twisted by about 70–80°, with one amino lone pair conjugating with the ring. However, this final optimized geometry is suspect since it has been noted[25] that the MINDO/3 method fails to reproduce the energetics of intermolecularly H-bonded systems and probably intramolecularly H-bonded systems as well. Therefore it is unlikely that in its present parameterization the MINDO/3 method could be used to provide accurate geometries or heats of formation for H-bonded ions such as those from **20-22**.

(v) Anomalies and Uncertainties. There are a few points in Figure 1 which deviate from the triple line by about 1 kcal/mol. While the deviation is small, it is somewhat disturbing in the case of benzoquinuclidine (**24**) since this should be a molecule whose structure opposes large changes in geometry on protonation. One might suggest that **24** is ring protonated; however, the orthogonal N lone pair would not be able to interact with the positive charge. Alternatively, as was pointed out in section iv, even the rigid systems can have different amounts of geometric relaxation or protonation which cannot be probed by the E_B measurements.

Although the present work demonstrates that large deviations in the E_B vs. $\Delta G°$ correlations can be found for some special systems, one might wonder in some unkown system which of these two possible reasons was responsible for an observed deviation. For molecules in which there is only one possible site for protonation such as simple olefins, amines, ketones, aldehydes, ethers, etc., the most likely source of deviation would be attributable to geometric changes occurring on protonation. On the other hand, for molecules which contain two possible sites for protonation such as anilines, one cannot rigorously attribute the deviation to a single factor, although other available evidence might allow one to favor a particular factor. Further work will be required before this latter dilemma can be resolved.

IV. Experimental Section

X-ray photoelectron spectra were obtained with a MacPherson 36 ESCA spectrometer equipped with a Mg Kα_{12} photoionization source using gaseous samples intimately mixed with a neon calibrant. In some cases, N_2 gas was also introduced along with the sample and neon to check the linearity of the spectrometer. In these cases, the $N_2$1s E_B value was found to be 410.0 ± 0.03 eV, experimentally identical with that reported.[23] Values reported are the averages of at least three consecutive runs and were computer deconvoluted as previously published.[26] Involatile samples were introduced into the target chamber with a heated inlet assembly.[1h] Compounds other than those identified below were commercial samples and were purified by standard methods prior to use.

Compounds **17**,[27] **18**,[27] **24**,[28] and **33**[29] were prepared and purified according to published procedures. Compounds **19–22** were kindly provided by Professor P. Kebarle.

Acknowledgments. The authors thank the University of Alberta and the National Science and Engineering Council of Canada for their support of this work. Helpful discussions with Professor P. Kebarle and private communications with Professors J. Beauchamp and R. W. Taft are also acknowledged, as are the helpful suggestions of the referees.

Note Added in Proof. Professor R. W. Taft has recently communicated to us a gas-phase basicity value for formamide which is 3.6 kcal/mol, midway between our two predicted values.

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(25) (a) Zielinski, T. J.; Breen, D. L.; Rein, R. *J. Am. Chem. Soc.* **1978**, *100*, 6266–6267. (b) Klopman, G.; Andreozzi, A.; Hopfinger, A. J.; Kikuchi, O.; Dewar, M. J. S. *Ibid.* **1978**, *100*, 6267–6268.

(26) Brown, R. S.; Allison, D. A. *J. Am. Chem. Soc.* **1977**, *99*, 3568–3572.

(27) Horning, C. H.; Bergstrom, F. W. *J. Am. Chem. Soc.* **1945**, *67*, 2110–2111.

(28) Meisenheimer, J.; Finn, O.; Schneider, W. *Ann.* **1920**, *420*, 219–239.

(29) Beak, P.; Bonham, J.; Lee, J. T. *J. Am. Chem. Soc.* **1968**, *90*, 1569–1582.