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Correlations between Core Photoionization Energies (E_B 1s) and Gas-Phase Basicity. A General Method for Determining Sites of Protonation and Intramolecular Ion Reorganization Energies

J. M. Buschek, F. S. Jørgensen,[‡] and R. S. Brown*

Contribution from the Department of Chemistry, University of Alberta,
Edmonton, Alberta, Canada T6G 2G2. Received February 1, 1982

Abstract: Based on earlier studies which showed that a correlation between 1s core electron binding energies and gas-phase basicity is expected to hold if both the site of photoemission and H^+ attachment are the same and large geometry changes do not occur on protonation, the present study focuses on utilizing such correlations to determine ion structure. For several bifunctional amines, not only can the site of protonation be determined with certainty but a semiquantiative assessment of the energy preference for that site can be obtained. For example, even though the intrinsic basicities of $(CH_3)_2NH$ and pyridine are the same within experimental error, covalent attachment of the two groups to form 2-, 3-, or 4-dimethylaminopyridine generates species in which N-protonation is favored by 13.5, 11.7, and 21.1 kcal/mol, respectively, over substituent protonation. Utilizing the X-ray (PES) methodology, we have extended the functional group classes for which the site of protonation can be determined to include amines, pyridines, carbonyl-containing species, and nitriles. Also presented is a further application of the coupled use of X-ray PES and gas-phase basicity data to determine the energetics of internal solvation of a bifunctional molecule which on protonation reorganizes geometrically to stabilize the ion state by internal H-bonding. X-ray PES, because it is a fast technique, is an ideal method for determining how the electronic (inductive and polarization) effects of a remote substituent influence the intrinsic basicity of a molecule in its ground-state geometry. The difference between this hypothetical intrinsic basicity and the experimentally determined value reflects the energy associated with nuclear reorganization in the ion state.

I. Introduction

It is now well established experimentally that a close relationship exists between the ability of a specific center of a molecule isolated in the gas phase to support charge generated by either H^+-attachment or inner-shell electron removal (eq 1). Initial work by Martin and Shirley[1a] and independently by Davis and Rabalais[1b] noted the formal similarity of the two processes and showed a linear correlation between the core electron binding energy (E_B) and gas-phase proton affinity (PA) within a well-defined series of bases. Subsequently, many additional examples were presented for molecules containing such diverse elements as N, O, P, S, and As.[2] Although it now appears that E_B vs. basicity correlations can be expected to hold only for a homologous series of bases, somewhat more general relationships between "lone-pair" ionization potentials and gas-phase PA's have been observed,[3] particularly if the adiabatic IP of a valence orbital localized at the site of protonation is considered.

$$\textcircled{+B}: + e^- \xrightarrow[E_B]{h\nu} \textcircled{:B}: + B_1H^+ \overset{K_{eq}}{\rightleftarrows} \textcircled{:B}-H^+ + B_1: \qquad (1)$$

1s "hole state"

$$\Delta G^\circ = -RT \ln K_{eq}$$
$$PA = -\Delta H^\circ \text{ (relative to a standard base)}$$

Recently we examined in some detail circumstances under which the E_B vs. gas-phase ΔG° or ΔH° correlation breaks down.[4] Such is the case (i) if the site of photoemission and protonation differ, and (ii) if large geometry changes occur on protonation which cannot be probed by the instantaneous photoemission process.[2] Further analysis would indicate that coupled use of X-ray photoelectron spectroscopy and methods to determine gas-phase basicities can provide information which cannot directly be obtained from either technique. In principle both the site of protonation of a molecule and the energetics of ion reorganization to accommodate the charge could be probed. Aside from our own work[4,5] a few other studies indicated the utility of this approach in determining the site of H^+-attachment in such bifunctional molecules as carboxylic acids and esters,[2f,g] C═O,[2d] pyrrole,[2c] and substituted anilines.[5] Furthermore, in the optimum cases, a quantitative assessment of the energy preference (in terms of ΔG° or ΔH°) of one site over another can be obtained,[2d,4,5] that information being valuable for testing the conclusions of molecular orbital calculations.

In the following, we address the general utility of this approach in determining not only the site of protonation of several molecules in the gas phase, but the energy advantage of H^+-attachment at that site. Secondly, we address the question of the energetics of internal solvation of a bifunctional molecule (:X⁓Y:) which on protonation can intramolecularly cyclize to stabilize the charged species.

II. Experimental Section

Nitrile and amine N_{1s} binding energies were determined with a MacPherson 36 ESCA electron spectrometer at ambient temperatures using Al and Mg Kα X-rays. Absolute binding energies are referenced to an internal standard of N_2 gas ($N_{1s}E_B$ = 409.93 eV[6]) or neon Auger line of 804.56 eV kinetic energy[6a] as previously described.[2e] Oxygen O_{1s}

[‡] H. C. Ørsted Institute, University of Copenhagen, DK-2100, Copenhagen, Denmark.

(1) (a) Martin, R. L.; Shirley, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 5299-5304. (b) Davis, D. W.; Rabalais, J. W. *Ibid.* **1974**, *96*, 5305-5310.

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E_B values were determined using Mg Kα X-rays and calibrated against an internal O_2 standard ($O_{1s}E_B$ = 543.55 eV for the strong line[7]).

Commercial samples were employed and purified by distillation. Halogen-containing amines were liberated from their commercially available HCl salts by treatment with saturated KOH, and distilled prior to use. Binding energy data were least-squares analyzed[8] assuming Gaussian peak shapes, and the reported values are the averages of at least three to five consecutive determinations in which the data collection sequence alternated between the co-introduced calibrant and sample.

III. Results

N_{1s} E_B and existing $\Delta G°$ and PA values are presented in Table I. Pyridine N_{1s} E_B data are abstracted from ref 2e, the associated amino-group values being presented in the table for the first time. The N_{1s} ionization region for the 2- and 3-aminopyridines consists of a single broad band (half-width ~ 1.9–2.0 eV) which was deconvoluted into two equal intensity peaks, the positions of which are presented to an estimated precision of ±0.1 eV although in general all other reported values have precisions of ±0.03 eV or better.

Basicity values are abstracted from the literature.[9,10] In so far as is possible for a given correlation, we have used values determined in a single laboratory to minimize cross-referencing errors. Presented in Table II are parameters describing the linear correlations between E_B and both $\Delta G°$ or $\Delta H°$ values for N-containing bases such as pyridines, primary and tertiary amines, and nitriles, in addition to those for carbonyl-containing species such as esters, acids, ketones, aldehydes, and amides. Much of the latter O_{1s} E_B data come from published work originating in Thomas' laboratory,[2g] those values agreeing excellently with our own where comparison is possible.

From each of the correlation lines it is possible to predict a basicity or proton affinity given an experimental E_B 1s value provided two fundamental criteria are satisfied, namely, that the site or protonation and photoemission are the same, and that large molecular reorganization does not occur on proton attachment. Of course, following protonation all molecules must respond electronically and geometrically to accommodate the charge; however, for a given series this latter expected reorganization is incorporated into the correlation as an upward deviation in the positioning of the best fit line over what it would be in the absence of nuclear reorganization. If for an unknown base a larger geometry change occurs than for the compounds used to define the basis set, this will be evident as a substantial upward deviation from the correlation line, the magnitude of the deviation reflecting the additional geometric stabilization. Since the relative basicity and E_B 1s data are each probably good to ±1 kcal/mol, the correlation lines should be considered accurate to ±2 kcal/mol. In view of this uncertainty, the following discussion will focus on deviations between predicted and observed basicities which are outside this limit.

IV. Discussion

A. At this point it is well to consider that Shirley's[1a] and Rabalais'[1b] original thesis concerning the E_B/basicity relationship considered that the enthalpy of core photoemission should be related to the enthalpy of protonation so that in the strictest sense one should compare E_B and proton affinities. In the great majority of cases, it is only the $\Delta G°$ values which are experimentally determined from an equlibrium situation involving proton transfer from one base to another in the gas phase. Proton affinity or $\Delta H°$ values are then calculated from the experimental $\Delta G°$ terms under the assumption that the major entropic contributions are those due to changes in the rotational degrees of freedom in the two bases.[9,10] Since the $\Delta S°$ values are based on changes in the rotational symmetry numbers, with the neglect of freezing or unfreezing of internal rotations during proton transfer, this is the most serious fault of such an approach.[14] We have in the past used only the experimental $\Delta G°$ values in our correlations;[2e,4] however, since these are in general less than 1 kcal/mol different from the calculated $\Delta H°$ values, either can be used without introducing large errors into the conclusions.

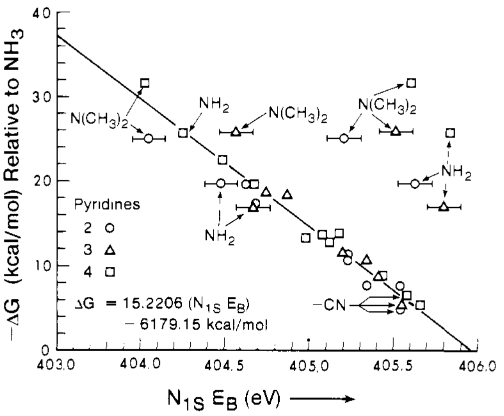

Figure 1. N_{1s} E_B vs. $\Delta G°$ correlation for 2-, 3-, and 4-substituted pyridines (binding energy data from ref 2e; basicity data from ref 9). Error bars due to deconvolution uncertainties of 0.1 eV are placed on the 2- and 3-amino (dimethylamino) E_B values. Shaded symbols represent amino N ionization.

In cases where large changes in internal rotation accompany the proton transfer (for example, when internal solvation occurs to produce stable cyclized ions), greater entropic corrections are to be expected since these must reflect freezing of the CH_2 rotations in the ion state. Aue and Bowers' original approach[13] to calculate the PA in such cases assumed that closure from an open-chain to cyclic entity could be approximated by the thermodynamic parameters for the corresponding hypothetical alkane ⇄ cycloalkane equilibrium.[9,13] Experimental values for several α,ω-substituted amines have been provided by Kerbarle[15] and Meot-Ner et al.[12] and are derived from the temperature-dependent van't Hoff plots for various proton-transfer equilibria. In general, agreement between Aue and Bowers' calculated $T\Delta S°$ terms[9] and the experimental ones of Meot-Ner et al.[12] is excellent, although these deviate somewhat from those of Yamdagni and Kebarle.[15] In Table I, we have included both calculated[9] and experimental[12] $\Delta H°$ values for our correlations, although we will concentrate more heavily on conclusions drawn from the experimental $\Delta G°$ numbers.

Determination of the sites of protonation and hence gas-phase ionic structure is difficult to do by direct experimental observation. This is because the concentrations of ions produced in the gas phase are far too low to allow their detection by normal optical techniques. Recent developments such as photodissociation spectroscopy[16] and collisional activation mass spectrometry[17] promise to yield valuable information about isolated ions although these techniques are still in their infancy and can hardly be considered routine.

Often, one can determine positions of protonation in bifunctional molecules by D-labeling experiments in which (following eq 2)

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[7] Davis, D. W.; Hollander, J. M.; Shirley, D. A.; Thomas, T. D. *J. Chem. Phys.* **1970**, *52*, 3295–3296.

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[11] Finn, P.; Pearson, R. K.; Hollander, J. M.; Jolly, W. L. *Inorg. Chem.* **1971**, *10*, 378–381.

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[14] For a discussion of this point in terms of acid dissociation in the gas phase, see: Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1–9.

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[16] (a) Dunbar, R. C.; Kim, M. S.; Olah, G. A. *J. Am. Chem. Soc.* **1979**, *101*, 1368–1370. (b) Dunbar, R. C. *Ibid.* **1975**, *97*, 1382–1384. (c) DeFrees, D. J.; Hehre, W. J.; McIver, R. T. *Chem. Phys. Lett.* **1976**, *42*, 564–566. (d) Bomse, D. S.; Berman, D. W.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3967–3971, and references therein.

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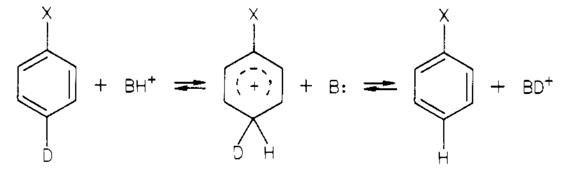


(2)

a D$^+$ may be removed from a given position only if H$^+$ had been transferred to it.[18] For example, by studying the reaction of phenol-*O-d* with a variety of bases of differing PA's, DeFrees et al.[18c] determined that ring protonation is favored by some 15 kcal/mol over oxygen protonation.

In the absence of experimental data one can alternatively resort to molecular orbital calculations of isodesmic proton-transfer reactions to determine the site and energetics of protonation. Although suggestive, since these are generally done using nonoptimized geometries to reduce computational costs, calculated differences of a few kcal/mol might be considered suspect.[19]

B. Pyridines. Shown in Figure 1 is the best-fit correlation between N$_{1s}$ E_B and $\Delta G°$ values for all pyridines, the regression parameters being given as entry 4a in Table II. Inspection of all data shows considerable scatter as is evidenced by the overall correlation coefficient of 0.9880, but it appears that substituents at each of the 2, 3, and 4 positions have their own particular correlations so that a family of lines is generated. Since aminopyridines **2–5** show a single broad N$_{1s}$ band encompassing both nitrogen ionizations, we have placed horizontal error bars of ±0.1 eV on the deconvoluted E_B values and have not included these in defining the overall regression. The 4-amino derivatives **6** and **7** each show two well-separated bands, so the associated E_B values are considered to be more accurate. In all cases, the value assigend to the ring nitrogen[20] is the one at lowest binding energy and is seen to lie close to the best fit line. This would clearly indicate that protonation in all cases occurs at the pyridine nitrogen. Should protonation occur at the amino substituent, we could predict the expected $\Delta G°$ by inserting the appropriate amino of dimethylamino N$_{1s}$ E_B into entries 5a or 6a (Table II), respectively. Having done this, one sees that the predicted basicities are between 10 and 25 kcal/mol lower than those observed, not only corroborating that ring protonation is favored, but also providing an assessment of the energy advantage of the latter site.

In the case of the 2-, 3-, and 4-cyanopyridines **8–10**, insertion of the ring N$_{1s}$ data into the appropriate equation in Table II (entries 1a, 2a, and 3a, respectively) gives predicted basicities of −6.1, −6.0, and −6.2 kcal/mol, in excellent agreement with those observed verifying that these too are ring protonated. This result can be corroborated by inserting the nitrile N$_{1s}$ E_B value into either entry 7a, 7b, or 8a (vide infra). In general, cross referencing using binding energies from the two potential sites provides consistent and valuable corroboration.

C. Nitriles. The correlation between nitrile N$_{1s}$ E_B and $\Delta G°$ values is shown in Figure 2. Because of the wide structural variety within the series **11–26**, we have broken the correlation in Table II into two parts. The first includes a basis set consisting of nitriles whose common feature is variation of a single substituent at the α carbon (e.g., **14**, **16–18**, **20**, **21**, and **23**), these giving a rather good correlation for both $\Delta G°$ and $\Delta H°$. The second includes all nitriles except **15** and **26** since their site of protonation is to be determined. Clearly more scatter is seen which is likely due to the wider variation in structure. Basicity data from both Taft's[10] and Aue and Bowers'[9] compendia are included separately since there appears to be some discrepancy with those of Taft giving the larger slope.

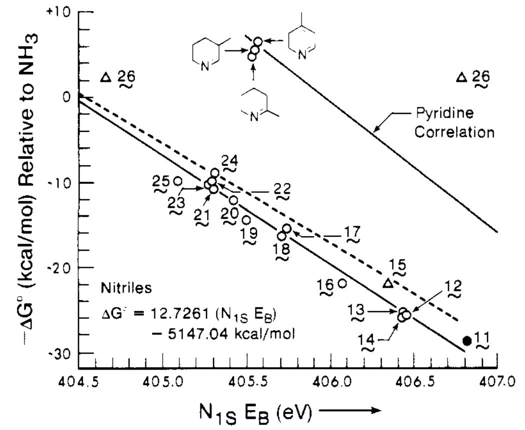
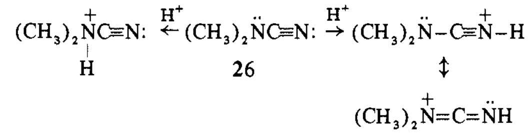


Figure 2. N$_{1s}$ E_B vs. $\Delta G°$ correlation for nitriles. Solid line and open symbols represent relationship using Taft's data (ref 10): broken line represents line position using Aue and Bowers' data (ref 9) (symbols not shown): shaded symbol, HCN; triangles, N$_{1s}$ E_B for **15** and **26** showing nitrile to be likely site of protonation.

Although it appears to be a general observation that substituent variations produce a somewhat greater effect on E_B 1s than on gas-phase basicity,[2,4] we note here that for the nitriles, N$_{1s}$ E_B is influenced nearly twice as much as $\Delta G°$, a fact which is currently under theoretical investigation.[21a]

Nitriles **15** and **26** are bifunctional in the sense that H$^+$-attachment could occur at two sites, giving ions whose gross structures would resemble those produced from protonation of one or the other group in the absence of the second.[21b] For **26**,



$$\underset{\displaystyle \mathrm{H}}{(\mathrm{CH_3})_2\overset{+}{\mathrm{N}}}\mathrm{C{\equiv}N{:}} \xleftarrow{\mathrm{H^+}} \underset{\displaystyle \mathbf{26}}{(\mathrm{CH_3})_2\ddot{\mathrm{N}}\mathrm{C{\equiv}N{:}}} \xrightarrow{\mathrm{H^+}} (\mathrm{CH_3})_2\ddot{\mathrm{N}}\mathrm{-C{\equiv}}\overset{+}{\mathrm{N}}\mathrm{-H} \;\updownarrow\; (\mathrm{CH_3})_2\overset{+}{\mathrm{N}}\mathrm{{=}C{=}}\ddot{\mathrm{N}}\mathrm{H}$$

simple resonance arguments suggest that nitrile protonation would be favored since the charge can be delocalized to the amino group, while no such delocalization can occur if the amino group is protonated. Here the N$_{1s}$ ionization region shows two distinct bands separated by 2.1 eV, the lower energy one at 404.66 eV being assigned to the nitrile.[22] Insertion of that value into entries 7b or 8a (Table II) yields predicted basicities of 2.7 and 1.6 kcal/mol less than NH$_3$. That the observed value of −2.2 kcal/mol

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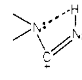
(18) (a) Freiser, B. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 6893–6894. (b) Martinsen, D. P.; Buttrill, S. E. *Org. Mass Spectrom.* **1976**, *11*, 762–772. (c) DeFrees, D. J.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 3853–3854.

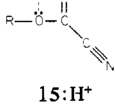
(19) See, for example, the site of protonation of aniline: Pollack, S. K.; Devlin, J. L., III; Summerhays, K. D.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4583–4584.

(20) In all cases it can be anticipated that the amino group should reduce the ring N$_{1s}$ E_B value from that of pyridine itself (404.94 eV^{2e}). Conversely, the effect of the somewhat electronegative pyridyl substituent on the amino N$_{1s}$ E_B should be to increase the value relative to that in aniline (405.45) or dimethylaniline (405.11 eV)^4 which is as observed.

(21) (a) Buschek, J. M.; Jørgensen, F. S.; Brown, R. S., unpublished work. (b) For nitriles **15** and **26** it might be envisioned that H$^+$ attachment at one sight might involve the electron pairs at the remote site to in effect "chelate" the proton and distort the geometry of the resultant ion. Should this, in fact, be the case, determination of the site of protonation using the X-ray PES methodology adumbrated in the text would lead to ambiguous conclusions. We are, however, convinced that any cyclic ions as would be produced by protonation of either **15** or **26** would necessitate severe strain within the four-membered cycles and/or an unfavorable localization of (+) charge in an sp^2-type orbital analogous to a vinyl cation, which could not be recouped by the internal solvation, i.e.,

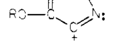


26:H$^+$



15:H$^+$

or



15:H$^+$

Experimental support for these conclusions comes from the fact that the nitrile N$_{1s}$ E_B values for **15** and **26** are sufficiently close to the linear regression lines defined by all other nitriles (in which remote functional groups are absent) that one need not invoke any "special" stability to the ions.

(22) The effect of the (CH$_3$)$_2\ddot{\mathrm{N}}$–group on C≡N ionization should be to substantially facilitate core electron removal so that the latter's N$_{1s}$ E_B should be among the lowest for nitriles. Conversely, the C≡N group should restrict ionization of the (CH$_3$)$_2\ddot{\mathrm{N}}$– core electrons relative to those of dimethylamine (404.9 eV^{6a}).

Table I. $N_{1s}E_B$, $\Delta G°$, and $\Delta H°$ Values Relative to NH_3 [a]

	compound	$N_{1s}E_B$ (eV)			
		pyridines[b,c]			
		pyridine N	amino N	$-\Delta G°$ (kcal/mol)	$-\Delta H°$ (kcal/mol)
1	pyridine	404.94		16.2	15.4
2	2-amino-	404.48	405.63	19.6	18.8
3	2-dimethylamino-	404.05	405.21	25.0	24.2
4	3-amino-	404.67	405.80	16.8	16.0
5	3-dimethylamino-	404.57	405.52	25.7	24.9
6	4-amino-	404.26	405.84	25.6	24
7	4-dimethylamino-	403.92	405.61	31.5	30.7
8	2-cyano-[c]	405.54	405.54	4.7	3.9
9	3-cyano-[c]	405.55	405.55	5.3	4.5
10	4-cyano-[c]	405.58	405.58	6.4	5.6
		nitriles[d]			
11	H-	406.81[e]		−28.8 (−25.3)	−29.6 (−26.9)
12	Cl-	406.45		−25.7 (−22.7)	−26.5 (−23.5)
13	Cl_3C-	406.44		−25.6 (−22.5)	−26.4 (−23.3)
14	$N{\equiv}CCH_2$-	406.43		−25.8 (−23.2)	−26.6 (−24.0)
15	EtO(C=O)-	406.34 (539.1, 540.5)[f]		−22.0 (−20.6)	−22.8 (−21.4)
16	$ClCH_2$-	406.07		−22.0 (−19.3)	−22.8 (−20.1)
17	CH_3-	405.74 (405.6)[g]		−15.5 (−13.3)	−16.3 (−14.1)
18	$ClCH_2CH_2$-	405.71		−16.4 (−14.1)	−17.2 (−14.9)
19	$CH_2{=}CH$-	405.50 (405.42)[l]		−14.5 (−12.4)	−15.3 (−13.2)
20	CH_3CH_2-	405.42 (405.3)[g]		−12.1 (−11.4)	−12.9 (−12.2)
21	*n*-Pr-	405.30		−10.8 (−10.4)	−11.6 (−11.2)
22	*i*-Pr-	405.29		−9.9 (−8.1)	−10.7 (−8.9)
23	*n*-Bu-	405.28		−10.2 (−8.4)	−11.0 (−9.0)
24	c-Pr-	405.31		−8.9 (−7.1)	−9.7 (−7.9)
25	Ph-	405.09 (405.0)[g]		−9.9	−10.7
26	$(CH_3)_2\ddot{N}$-	404.66 (406.78)[h]		2.2	1.6
		bifunctional amines			
27	$H_2N(CH_2)_2NH_2$	404.96		19.1 (19.3)[j]	21.5 (19.5-20.8)[j]
28	$H_2N(CH_2)_3NH_2$	404.89		24.5 (24.4)[j]	27.7 (27.5;[k] 28.3[j])
29	$H_2N(CH_2)_4NH_2$	404.90		27.5 (28.2)[j]	33.1 (32.5[j])
30	$H_2N(CH_2)_5NH_2$	404.89		25.5	30.8
31	$H_2N(CH_2)_6NH_2$	404.84		25.5	31.6
32	$H_2N(CH_2)_2OH$	405.30		16.0[j]	15.7[j]
33	$H_2N(CH_2)_3OH$	405.28		19.6 (19.7)[j]	22.8 (22.8)[j]
34	$H_2N(CH_2)_2OCH_3$	404.88		15.9	18.3
35	$H_2N(CH_2)_3Cl$	405.11		13.6	17
36	$H_2NCH_2CF_3$	405.87		−1.5	−1.7
37	$(CH_3)_2N(CH_2)_3N(CH_3)_2$	404.53		33.8	37
38	$(CH_3)_2N(CH_2)_4N(CH_3)_2$	404.53		35.3	40.9
39	$(CH_3)_2N(CH_2)_6N(CH_3)_2$	404.53		32.9	44

[a] E_B values have precision of ±0.03 eV except for **2** and 4 which are ±0.1 eV. [b] Pyridine $N_{1s}E_B$ values from ref 2e; $\Delta G°$ and $\Delta H°$ values from ref 9. [c] N_{1s} ionization region exhibits a single narrow (half-width 1.45-eV) band. [d] Nitrile $\Delta G°$ and $\Delta H°$ from Taft et al;[10] values in brackets from ref 9. [e] Reference 11. [f] O_{1s} ionizations assigned to C=O and C−OEt oxygens, respectively (precision ±0.1 eV, calibrated against internal O_2 standard of 543.55 eV[7]). [g] Fujikawa, T.; Ohta, T.; Kuroda, H. *Bull. Chem. Soc. Jpn.* 1976, *49*, 1486–1492. [h] Assigned to tertiary amino nitrogen. [i] Data of Aue et al.[9] $\Delta H°$ is derived from $\Delta G°$ assuming the $T\Delta S°$ term can be estimated from the corresponding alkane $\rightleftarrows$ cycloalkane equilibria. [j] Reference 12, relative to NH_3. PA values in this work are derived from temperature studies. [k] Reference 13, relative to NH_3. [l] Unpublished data from laboratory of W. L. Jolly, Berkeley, Calif.

(greater than NH_3) is roughly 4–5 kcal/mol different from the predicted values likely reflects the long extrapolation of the rather poorly defined lines and not an alternative protonation site. This is supported by considering that if **26** had been amino-protonated, its basicity predicted by the use of entry 6a would be 7.4 kcal/mol less than NH_3, fully 10 kcal/mol less than that observed. It is likely that this material belongs to an independent subfamily of nitriles since it is structurally quite different from the others, but at present this cannot be tested since basicity data for nitriles are somewhat limited. It is also possible that, during C≡N pro-

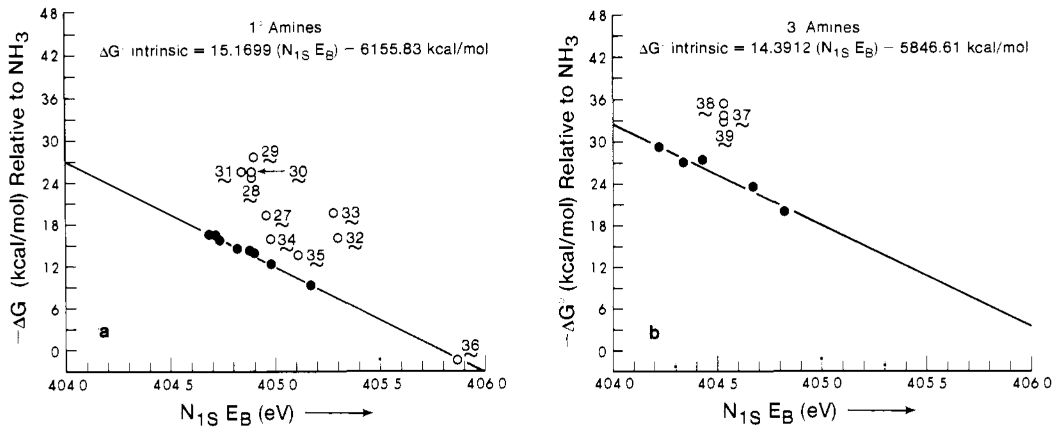


Figure 3. (a) N_{1s} E_B vs. $\Delta G°$ correlation for primary amines. Vertical deviation of symbol from the line represents $\Delta G°$ reorganization (see text). (b) N_{1s} E_B vs. $\Delta G°$ correlation for tertiary amines.

Table II. Parameters for Linear Correlation of E_B and $\Delta G°$ or $\Delta H°$ Values Relative to NH_3 Defined as Energy (kcal/mol) = a(kcal/eV)E_B(eV) − b[a]

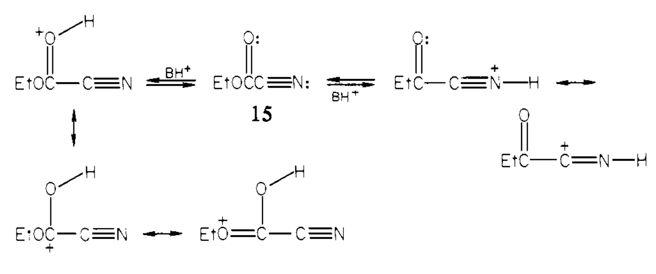
entry no.	base	energy term	a	$-b$	correlation coefficient
1a	pyridines, 2-subst[b,c]	$\Delta G°$	14.3811	5838.21	0.9718
1b	pyridines, 2-subst[b,c]	$\Delta H°$	14.3811	5837.41	0.9718
2a	pyridines, 3-subst[b,c]	$\Delta G°$	16.6725	6767.61	0.9892
2b	pyridines, 3-subst[b,c]	$\Delta H°$	16.6725	6766.80	0.9892
3a	pyridines, 4-subst[b,c]	$\Delta G°$	15.2463	6189.77	0.9835
3b	pyridines, 4-subst[b,c]	$\Delta H°$	15.0541	6111.09	0.9904
4a	pyridines, all subst[b,c]	$\Delta G°$	15.2206	6179.15	0.9880
4b	pyridines, all subst[b,c]	$\Delta H°$	15.0717	6118.03	0.9872
5a	primary amines[b,d]	$\Delta G°$	15.1699	6155.83	0.9969
5b	primary amines[b,d]	$\Delta H°$	15.1701	6155.70	0.9960
6a	tertiary amines[b,d]	$\Delta G°$	14.3912	5846.61	0.9806
6b	tertiary amines[b,d]	$\Delta H°$	14.2455	5787.10	0.9774
7a	nitriles[e,f]	$\Delta G°$	13.7794	5574.31	0.9900
7b	nitriles[e,g]	$\Delta G°$	12.7261	5147.04	0.9895
7c	nitriles[e,f]	$\Delta H°$	13.7732	5571.00	0.9946
7d	nitriles[e,g]	$\Delta H°$	12.7261	5146.24	0.9895
8a	nitriles[g,h]	$\Delta G°$	11.7034	4734.29	0.9856
8b	nitriles[g,h]	$\Delta H°$	11.9625	4838.63	0.9882
9a	carbonyls[i]	$\Delta G°$	16.352	8791.28	0.995
9b	carbonyls[i]	$\Delta H°$	15.2438	8194.47	0.9948
10a	amides[j]	$\Delta G°$	14.7774	7945.29	0.997
10b	amides[b,j]	$\Delta H°$	15.2438	8197.47	0.9949

[a] Parameters derived from linear least-squares analysis. [b] $\Delta G°$ and $\Delta H°$ values from ref 9. [c] N_{1s} E_B values from ref 2e. [d] N_{1s} E_B values from a compendium of Bakke, A. A., Chen, H.-W.; Jolly, W. L. *J. Electron Spectrosc. Relat. Phenom.*, 1980, *20*, 333–666. [e] $\Delta G°$ and $\Delta H°$ values from Taft, R. W., private communication, and ref 10. [f] Includes only nitriles having variation of a single substituent at the α carbon, i.e., 14, 16, 17, 18, 20, 21, and 23 (Table I). [g] All nitriles in Table I except 15 and 26. [h] $\Delta G°$ and $\Delta H°$ values from ref 9. [i] O_{1s} E_B values for esters, acids, ketones, and aldehydes from ref 2g; amide values from ref 4. [j] Amide O_{1s} E_B values from ref 4; $\Delta G°$ value for formamide is 3.6 kcal/mol less basic than NH_3: Taft, R. W., private communication.

tonation, the dialkyl amino group undergoes considerably flattening toward sp^2 hybridization to maximize the long-pair delocalization in the ion. This too would cause an upward deviation from a given correlation.[4,5] Nevertheless, even though the agreement between the observed basicity and that predicted on the basis of entries 7b or 8a is not as close as one would like, we consider **26** to be nitrile protonated.

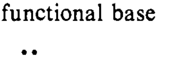
Although the 2-, 3-, and 4-cyanopyridines (**8–10**) were considered in the last section to be ring protonated, it is instructive to verify that conclusion by inserting their N_{1s} E_B values into the generalized nitrile equations. Since the N_{1s} ionization region for each of **8–10** shows a single sharp band, both ring and nitrile nitrogens have equivalent values. Entries 7b (8a) give predicted basicities of 13.9 (11.9), 14.0 (12.0), and 14.4 (12.7) kcal/mol less than NH_3. This indicates that ring protonation in all cases is favored by some 18–20 kcal/mol over nitrile protonation, the deviation being illustrated graphically in Figure 2.

Finally we consider ethyl cyanoformate (**15**). Simple resonance



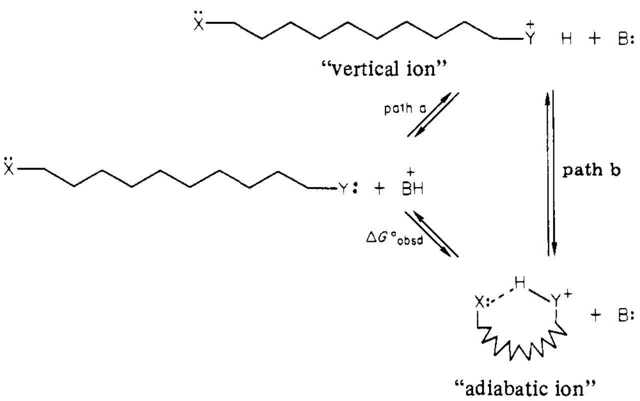
motions do not allow a ready choice of the site of H^+-attachment. If anything ester protonation might be considered more likely because of involvement of the ethoxy oxygen. Here again application of the method provides a simple evaluation since the nitrile N_{1s} E_B of 406.34 eV leads to predicted basicities of 24.1 and 21.3 kcal/mol less than NH_3 (depending upon whether entry 7b or 8a is used) in agreement with the experimental value of 22.0 kcal/mol. Although nitrile protonation is implied, to test for the possibility of C=O attachment, the observed O_{1s} E_B of 539.10 eV and entry 9a, which is derived for esters, amides, ketones, aldehydes, and acids, leads to a predicted basicity of 24.1 kcal/mol less than NH_3. In this case, the closeness of the predicted O and N basicities and the observed value would suggest that both sites can be protonated with equal likelihood. Although once again we are limited by extant basicities, it is conceivable that alteration of the alkoxy group substituent in a series of cyanoformates related to **15** would lead to a preference of one or the other sites as was evident in the case of meta-substituted anilines.[5]

D. Intramolecular Stabilization. Of the many structural features which influence basicity, intramolecular stabilization of the protonated site by a remote substituent possessing nonbonded electrons has received increasing attention[9,12,13,15] and appears ideally suited to analysis by the X-ray PES methodology. We consider as in Scheme I that H^+-attachment can be broken into two hypothetical steps. In the first step following path a, the proton is transferred to bifunctional base



to form a "vertical ion" whose geometry is not markedly different from that of the ground state. For this ion, the intrinsic basicity of Ÿ is determined by the rest of the molecule's ability to respond to protonation by inductive and polarization effects, but not by nuclear reorganization. Core photoemission from Ÿ is therefore the ideal probe for the intrinsic basicity since, although electronic response by inductive and polarization effects is allowed to stabilize the hole state, geometric reorganization is not.

Scheme I



In the second hypothetical step, following formation of the vertical ion, the molecule stabilizes itself by internal cyclization to form an intramolecularly H-bonded species (path b), thereby releasing energy in forming an adiabatic ion which is fully relaxed electronically as well as geometrically. Of course, in the true protonation process, the two hypothetical steps are inseparable since an equilibrium is established which is indicative of the lowest energy states of both substrate H^+ and BH^+ ions, so that the assessment of internal solvation energies cannot be made without additional assumptions. Such internal solvation would be expected if H-bonding in the cyclic ion state (adiabatic ion) more than compensates for whatever strain effects may be imposed by the structure; otherwise, the ion will remain open, or nearly so. Hence highly strained four-membered cyclic ions are anticipated to be open, while five and higher membered cycles should be attainable. Commonly, when the internal solvation of an α,ω-substituted amine is sought, its gas-phase basicity is compared with that of an aliphatic amine of "comparable polarizability", the difference being ascribed to internal solvation.[9,12,13,15] While it is generally true that remote substituents will have negligible inductive effects on the amine basicity unless unusual conformational preferences bring the two ends into proximity, such is surely not the case if substituent and amine are separated by only one to three intervening CH_2 groups. In these cases deciding what constitutes an amine of comparable polarizability becomes a difficult enough problem that the intrinsic basicity cannot be evaluated with any certainty, nor can the associated internal solvation. It is in just these cases that the photoionization methodology finds its greatest utility.

At this point one requires a set of reference lines which relates N_{1s} E_B and basicities for the amines to be considered. Some time ago, Martin and Shirley[2a] demonstrated that although the data for all amines could be fit to a single rough correlation, much better plots could be found for amines of the same general type. Hence primary, secondary, or tertiary amines generate a related family of correlations. Following this, we have presented in Table II the appropriate correlation lines for primary and tertiary amines (entries 5 and 6, respectively), with the basicity data being taken from Aue's compendium,[9] and core ionization energies from Jolly's tabulation.[23]

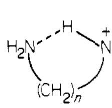
Given an experimental N_{1s} E_B, each of these equations should yield a predicted intrinsic basicity for the amine which reflects only the electronic effects of a remote substituent. Listed in Table III are the intrinsic basicities and PA's for H^+-attachment to a particular base to form its vertical ion, as well as the reorganization or internal solvation energies, calculated to be the difference between the observed adiabatic and vertical ion energies.

For the homologous series of diamines **27**–**31** it is clear that in terms of $\Delta G°$ the internal solvation attains a maximum value of ~14 kcal/mol for **29** with reduced values for the larger and smaller homologues. This undoubtedly reflects a compromise between ring strain and H-bond energy in the ion with the optimum situation being the seven-membered cycle **40c** in which

Table III. Calculated Energies of Protonation and Ion Reorganization (kcal/mol relative to NH_3)[a]

	calculated energies				observed energies	
base $\xrightarrow{H^+}$	vertical ion		reorganization $\longrightarrow$		adiabatic ion[b]	
	$-\Delta G°$	$(-\Delta H°)$	$-\Delta G°$	$(-\Delta H°)$	$-\Delta G°$	$(-\Delta H°)$
27	12.6	(12.4)	6.5	(9.1)	19.1	(21.5)
28	13.7	(13.5)	10.8	(14.2)	24.5	(27.7)
29	13.4	(13.3)	14.1	(19.8)	27.5	(33.1)
30	13.7	(13.5)	11.8	(17.3)	25.5	(30.8)
31	14.5	(14.2)	11.0	(17.4)	25.5	(31.6)
32	7.5	(7.3)	8.5	(8.4)	16.0	(15.7)
33	7.8	(7.6)	11.8	(15.2)	19.6	(22.8)
34	13.8	(13.6)	2.1	(4.7)	15.9	(18.3)
35	10.4	(10.1)	3.2	(6.9)	13.6	(17)
36	−1.1	(−1.4)	0.4	(0.3)	−1.5	(−1.7)
37	24.9	(24.4)	8.9	(12.8)	33.8	(37)
38	24.9	(24.4)	10.4	(16.5)	35.3	(40.9)
39	24.9	(24.4)	8.0	(19.6)	32.9	(44)

[a] Calculated vertical ion energies based on eq 5a,b and 6a,b.
[b] Experimental energies from ref 9.



40a, $n = 2$
b, $n = 3$
c, $n = 4$
d, $n = 5$
e, $n = 6$

the $N\text{---}H\text{—}N^+$ moiety can attain near-linearity. Further increases in ring size, while still providing a linear H bond have additional consequences in that an increasing number of CH_2 rotations must be restricted which should be reflected in a reduced value of $\Delta G°$ (reorganization). Since $\Delta H°$ (reorganization) is also seen to be maximized at the seven-membered cycle, and reduced by further expansion of the ring, transannular buttressing and methylene eclipsing interactions are evident which detract from the favorable enthalpy of the internal H bond.[13] Similar conclusions can be drawn for the tertiary amines **37**–**39**. In general, the reorganization energies determined by this approach are in excellent agreement with those given previously by Aue and Bowers[9,13] on the basis of comparison of the diamine values with those of a monoamine of comparable polarizability.

The situation for bases **32**–**36** is similar except that here one anticipates and observes much larger alterations of the amine intrinsic basicity by the electronegative substituents. For example, trifluoroethylamine (**36**) is predicted to have a basicity of 1.1 kcal/mol less than NH_3 in the absence of nuclear reorganization of its ion. That the observed basicity is 1.5 kcal/mol less than NH_3 indicates little or no nuclear reorganization in the ion and hence that a CF_3 unit β to an ammonium ion is incapable of H-bonding. For 3-chloro-1-propylamine (**35**) the situation is somewhat different in that although the γ-Cl reduces the intrinsic basicity relative to n-propylamine by 3–4 kcal/mol,[24] intramolecular cyclization of the ion provides a calculated 3.2-kcal/mol stabilization which exactly offsets the Cl inductive effect.

Amino alcohols **32** and **33** show a substantially reduced intrinsic basicity relative to the corresponding diamines (**27** and **28**) which in part reflects the increased inductive effect of O over N. There is, however, an additional complication in that these alcohols should exhibit pronounced intramolecular H-bonding in their ground states (**41**) which will have the consequence of further reducing the amine basicity since additional input of energy is required to break the H bond prior to (or concurrent with) proton attachment (eq 3). Ethanolamine (**32**) apparently exists completely in its

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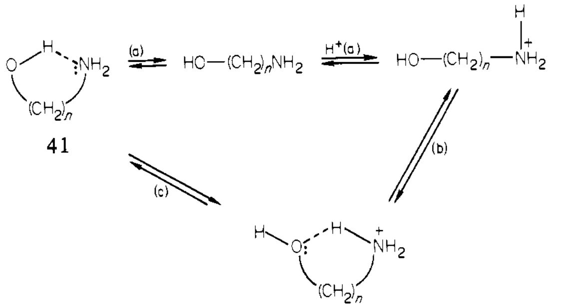
(23) Bakke, A. A.; Chen, H.-W.; Jolly, W. L. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 333–366; we thank Professor Jolly for providing us with a recent addendum to this tabulation.

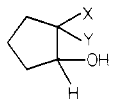
(24) $\Delta G°$ for n-$PrNH_2$ = −13.7 kcal/mol (relative to NH_3).[9]



(3)

OH---NH$_2$ H-bonded form in the gas phase,[25a,b] and, although an experimental gas-phase enthalpy appears not to be yet available, calculations place the H-bond energy to be between 2.4 and 3.2 kcal/mol.[25a,c] In solution this value is roughly 1.0 kcal/mol in favor of the OH---NH$_2$ gauche form.[26] In the gas phase, the analogue *N,N*-dimethylaminoethanol is estimated to have a H-bond energy of 4.9 kcal/mol.[27]

Again N_{1s} photoemission appears to be an ideal probe for the total hydroxyl effect on amine basicity or PA. Some time ago we determined by comparison of the N_{1s} E_B values for the trans and cis isomers of 2-aminocyclopentanol (**42a,b**) and 2-*N,N*-dimethylaminocyclopentanol (**42c,d**) that the effect of the OH---:N H bond was to raise the N_{1s} binding energy substantially.[8] For **42a,b** the difference was 0.19 eV (404.94 vs. 405.13 eV), while for **42c,d** it was 0.26 eV (404.64 vs. 404.90 eV)[8]. Solution studies indicated the H-bond energy of **42b** to be 1.9 kcal/mol with the OH---NH$_2$ form favored; unfortunately, a corresponding $\Delta H°$ for **42d** could not be obtained, but its $\Delta G°$ was estimated to be at least 3.4 kcal/mol.[28]



42a, X = H; Y = NH$_2$
b, X = NH$_2$; Y = H
c, X = H; Y = N(CH$_3$)$_2$
d, X = N(CH$_3$)$_2$; Y = H

If we assume that the cis/trans N_{1s} ionization differences of **42a,b** and **42c,d** reflect only the H-bond effect and the inductive effects of the OH on :N are approximately constant for both isomers, then insertion of the N_{1s} E_B data into the appropriate entries in Table II leads to predicted basicities of the trans isomers (**42b,d**) which are 2.9 and 3.7 kcal/mol greater than the cis isomers. This difference of 3 to 4 kcal/mol is attributable to the stabilization afforded to the ground states by the H bond and agrees well with the experimental $\Delta H°$ of H-bonding which in turn relates to the expected reduction in basicity. In other words, based on the above, it appears as if the N_{1s} E_B value reflects the energetics of the H bond within the experimental limitations of the data.

Thus while the predicted intrinsic proton affinities of **32** and **33** of −7.3 and −7.6 kcal/mol, respectively, reflect the net effect of the OH H bond on the ground state of each, the reorganizational energies of −8.4 and −15.2 kcal/mol reflect the net stabilization of the respective ion states. Here too the six-membered ring affords a larger ion stabilization than the five-membered cycle.

Since the methoxy derivative **34** is incapable of a similar H-bonding interaction in its ground state,[25] it shows a much larger intrinsic PA as expected. The reorganization energy of 4.7 kcal/mol reflects the ability of the CH$_3$O group to H-bond to the adjacent ammonium ion.

Conclusions

It is evident from the above that the combination of photoionization E_B and gas-phase basicity data can provide fundamental information not only about sites of protonation of a given molecule but also the energetics of ion reorganization subsequent to (or concurrent with) proton attachment. Although extant basicity data limit the correlations to those we have considered here, we anticipate that this should be a quite general method. A number of interesting types of molecules lend themselves easily to future study including enamines, vinyl ethers, hydrazines, and $-\ddot{X}-\ddot{Y}-$ species.

From the equations presented in Table II, it should be possible to predict reliable gas-phase basicity or proton affinity data for a given molecule falling into those classes, by simply determining an experimental core binding energy provided the site of protonation is known and ion reorganization does not contribute largely to the basicity.

Finally, based on the deviation of a given bifunctional amine from an E_B vs. basicity correlation line defined by an appropriate series of reference bases, one can assess accurately the reorganization energy of the ion. The real utility of this method comes from the fact that the core ionization provides an accurate probe of the effect of the substituent (both inductive and polarization) on the basicity for the ground-state geometry, but is too fast to be affected by nuclear reorganization.

Acknowledgment. The authors gratefully acknowledge financial assistance from the University of Alberta and Natural Science and Engineering Research Council of Canada.

Registry No. 1, 110-86-1; **2**, 504-29-0; **3**, 5683-33-0; **4**, 462-08-8; **5**, 18437-57-5; **6**, 504-24-5; **7**, 1122-58-3; **8**, 100-70-9; **9**, 100-54-9; **10**, 100-48-1; **11**, 74-90-8; **12**, 506-77-4; **13**, 545-06-2; **14**, 109-77-3; **15**, 623-49-4; **16**, 107-14-2; **17**, 75-05-8; **18**, 542-76-7; **19**, 107-13-1; **20**, 107-12-0; **21**, 109-74-0; **22**, 78-82-0; **23**, 110-59-8; **24**, 5500-21-0; **25**, 100-47-0; **26**, 1467-79-4; **27**, 107-15-3; **28**, 109-76-2; **29**, 110-60-1; **30**, 462-94-2; **31**, 124-09-4; **32**, 141-43-5; **33**, 156-87-6; **34**, 109-85-3; **35**, 14753-26-5; **36**, 753-90-2; **37**, 110-95-2; **38**, 111-51-3; **39**, 111-18-2.

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(25) (a) Penn, R. E.; Curl, R. F. *J. Chem. Phys.* **1971**, *55*, 651–658. Calculated $\Delta H°$ of −3.2 kcal/mol from point charge model. (b) Penn, R. E.; Olsen, R. J. *J. Mol. Spectrosc.* **1976**, *62*, 423–428. (c) Raudino, A.; Millefiori, S.; Zuccarello, F.; Millefiori, A. *J. Mol. Struct.* **1979**, *51*, 295–299, estimate the H-bond enthalpy in **32** to be 2.4 kcal/mol from calculations.

(26) Krueger, P. J.; Mettee, H. D. *Can. J. Chem.* **1965**, *43*, 2970–2977, report the $\Delta H°$ of H-bonding for **32** is −0.7 ± 0.2 kcal/mol in tetrachloroethylene. 2-Methoxyethylamine (**34**) apparently prefers an anti over gauche arrangement of the CH$_3$O and NH$_2$ groups by 1.6 ± 0.9 kcal/mol.

(27) Penn, R. E.; Birkenmeier, J. A. *J. Mol. Spectrosc.* **1976**, *62*, 416–422.

(28) Brown, R. S. *Can. J. Chem.* **1976**, *54*, 642–646.