A Molecular Orbital Study of Protonation. 2. Pyridine and the Diazines

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Abstract: Ab initio SCF calculations with minimal STO-3G and slightly extended 4-31G basis sets have been performed to determine the relative proton affinities of pyridine and the diazines. The experimental order (pyridine > 1,2-diazine > 1,3-diazine > 1,4-diazine) is reproduced at the 4-31G level. A correlation is found between increasing n orbital energy and increasing proton affinity of nitrogen bases, provided that the n orbitals are similar. The structures of the protonated ions show that the bond formed between the proton and the nitrogen atom has characteristics of a normal intramolecular covalent bond. Some comparisons are made of the proton affinities and hydrogen bonding abilities of nitrogen bases.

Recent experimental studies have shown that the relative proton affinities of bases in the gas phase may be significantly different from their relative proton affinities in solution.[1-3] Data for the following proton transfer reaction illustrate this quite dramatically:

$$NH_4^+ + C_5H_5N \rightleftarrows NH_3 + C_5H_5NH^+$$

The enthalpy changes are −15.8,[4] +4.7,[2] and +7.7[2] kcal/mol, for the reaction in the gas phase, in HSO_3F, and in H_2O, respectively. In order to understand the gas phase results and as a first step toward understanding the solution data, it is necessary to analyze and evaluate the factors which influence the proton affinities of bases in the gas phase. Ab initio molecular orbital calculations are particularly useful for such analyses, and several MO studies of proton affinities have been reported.[5-10] In this paper, the results of a molecular orbital study of the proton affinities of four isoelectronic nitrogen bases, namely pyridine, pyridazine (1,2-diazine), pyrimidine (1,3-diazine), and pyrazine (1,4-diazine) are presented. The proton affinities of these bases are compared with the computed proton affinities of other nitrogen bases and with experimental data. The computed results serve as a basis for analyzing the factors which influence the relative proton affinities of these compounds. Some comparisons are also made between the proton affinities and hydrogen bonding abilities of nitrogen bases.

Method of Calculation

Basis Sets. The ground-state wave functions for the nitrogen bases and the protonated ions have been described by single Slater determinants consisting of doubly occupied molecular orbitals. The molecular orbitals ψ_i are expressed as linear combinations of atomic basis functions ϕ_μ (the LCAO approximation)

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu$$

with the coefficients $c_{\mu i}$ determined variationally in the usual manner. Two sets of atomic functions have been used for the MO expansions, the minimal STO-3G basis set with standard scale factors[11] and the extended split-valence 4-31G basis set.[12]

Geometry Optimization. Optimized STO-3G geometries for the azabenzenes had been reported previously[13] and have been used in this study. With the structures of these bases held rigid, the structures of the protonated ions have been optimized at the STO-3G level in two protonation coordinates. The distance R between the proton and the proton-acceptor nitrogen atom has been optimized to ±0.01 Å. The angle θ between the H^+–N line and the principal axis of the base (the bisector of the C_6–N_1–X_2 angle, see Figure 1) has been optimized to ±1°. The computed proton affinity is the negative ΔE for the reaction $B + H^+ \rightarrow BH^+$.

It is well known that the minimal STO-3G basis set significantly overestimates proton affinities and the degree of charge transfer to the proton. To obtain more reasonable computed proton affinities requires that an extended basis set such as 4-31G be used for the calculations, although even with this basis set proton affinities are still overestimated by about 10%. In this study, the proton affinities of the nitrogen bases have also been computed with the larger 4-31G basis set, using the optimized structures determined at the STO-3G level. This procedure does introduce an error into the computed 4-31G proton affinities in addition to that due to the rigid monomer restriction. The energetic effects of these approximations have been investigated in protonated formaldehyde,[10] and relevant data are also available for H_3O^+.[5,10] These data, together with the good agreement between the relative proton affinities computed at the 4-31G level and experimental values, suggest that this approach is acceptable, particularly if trends in the proton affinities of a related series of bases are being determined as is the case here.[14]

Results and Discussion

The equilibrium structures of the protonated azabenzenes are reported in Table I. The structures of these ions are very similar, with little variation in the protonation coordinates R and θ. The N–H bond in these ions is highly directional, and the bond length is typical for N–H bonds. These characteristics of the N–H bond are similar to those of the O–H bond in protonated substituted carbonyl compounds, which exhibited nearly constant O–H bond lengths along a trigonal direction with respect to the carbonyl oxygen.[10] Thus, these data show that the bond between the proton and the proton-acceptor atom in protonated ions has the structural characteristics of a normal intramolecular covalent bond.

The computed proton affinities of the azabenzenes are also reported in Table I, along with the corresponding experimental data. As anticipated, the proton affinities are significantly overestimated at the STO-3G level, but are in reasonable agreement with experimental proton affinities at the 4-31G level. While both the STO-3G and 4-31G basis sets predict that pyridine is the strongest and 1,4-diazine the weakest base toward a proton, only at the 4-31G level are the relative proton affinities of the four azabenzenes (pyridine > 1,2-diazine > 1,3-diazine > 1,4-diazine) reproduced by the calculations. The STO-3G basis set fails to discriminate between the proton affinities of 1,2- and 1,3-diazine. This is rather surprising in view of the usual success of the STO-3G basis set in predicting relative proton affinities of related bases.[1,6,7,10]

It is apparent from both experimental and theoretical data that the strength of a particular acid–base interaction is de-

Table I. Structures and Energies of Protonated Azabenzenes

Base	STO-3G structure		$-\Delta E^a$	$-\delta\Delta E^b$	$-\Delta E^a$	$-\delta\Delta E^b$	$-\delta\Delta H^b$
	R, Å	θ, deg	STO-3G	STO-3G	4-31G	4-31G	(exptl)[c]
Pyridine	1.03	180	272.7	0.0	238.5	0.0	0.0 (218.1)[d]
1,2-Diazine	1.04	176	263.8	−8.9	231.4	−7.1	−4.3
1,3-Diazine	1.03	180	264.5	−8.2	228.9	−9.6	−9.5
1,4-Diazine	1.04	180	256.0	−16.7	220.6	−17.9	−11.7

[a] $-\Delta E$ for the reaction $B + H^+ \rightarrow BH^+$, in kcal/mol. [b] $-\delta\Delta E$ (and $-\delta\Delta H$) refer to the gas-phase reaction: $C_5H_5NH^+ + B \rightarrow C_5H_5N + BH^+$ and measure the proton affinity of B relative to pyridine. [c] Experimental data from R. W. Taft, private communication. [d] The gas-phase proton affinity of pyridine relative to a proton affinity of 202.3 kcal/mol for NH_3, reported in ref 3.

Table II. Proton Affinities and Related Properties of Azabenzenes[a]

Base	$-\delta\Delta E$	$Q(\mathrm{N})^b$	$Q(\mathrm{N}\pi)^b$	$\delta Q(\mathrm{N})^c$	$Q(\mathrm{H}^+)^c$	$\epsilon(\mathrm{N1s})^d$	$\epsilon(\mathrm{n})^d$
Pyridine	0.0	7.556	1.134	0.307	0.526	−423.1	−11.12
1,2-Diazine	−7.1	7.298	1.078	0.283	0.498	−424.5	−10.75
1,3-Diazine	−9.6	7.569	1.155	0.287	0.519	−423.4	−10.84
1,4-Diazine	−17.9	7.499	1.068	0.324	0.508	−424.2	−11.13

[a] Data from 4-31G calculations. [b] $Q(\mathrm{N})$ and $Q(\mathrm{N}\pi)$ are the Mulliken total and π electron populations of the nitrogen atoms in the bases. [c] $\delta Q(\mathrm{N})$ and $Q(\mathrm{H}^+)$ are the increase in the negative charge on the proton acceptor nitrogen atom and the amount of electron transfer to the proton, respectively, in the ions. [d] $\epsilon(\mathrm{N1s})$ and $\epsilon(\mathrm{n})$ are the 1s and n orbital energies (eV), respectively, in the bases.

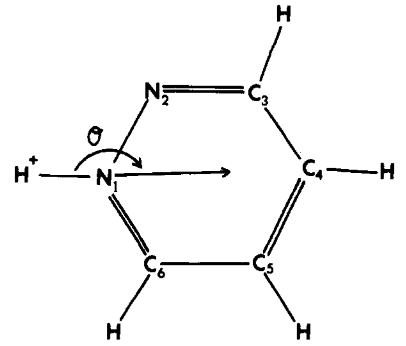

Figure 1. The structure of protonated 1,2-diazine.

termined not only by the nature of the acid and base individually, but also by the particular acid-base pair. These dependencies emerge because there are several factors which influence acid-base interactions, and their relative weightings may vary. Therefore, in studies of basicity it is advantageous to compare related bases to identify trends in a particular series and to isolate factors which are responsible for determining these trends. To this end, selected properties of the azabenzenes and the protonated ions are reported in Table II.

It is evident from the data of Table II that neither the total nor the π electron populations, determined from Mulliken population analyses,[15] correlate with the proton affinities of these bases. Rather, in the diazines in particular, these populations appear to reflect inductive effects of two nitrogen atoms 1,2-, 1,3-, and 1,4- to each other. It should be noted that this lack of correlation does not mean that the electrostatic interaction between the proton and the base is not an important factor in stabilizing these ions. Rather, the Mulliken populations may be too crude a measure to reflect small differences in electrostatic interactions, or the electrostatic interaction may not be the factor which determines the specific order of basicity in this series.[9]

As evident from Table II, no correlation exists between the nitrogen 1s orbital energies and the proton affinities of these nitrogen bases. However, the n orbital energies (the vertical n ionization potentials as approximated by Koopmans' theorem) do correlate with the relative proton affinities of the diazines. Beauchamp first noted a correlation between experimental ionization potentials and proton affinities of bases, and suggested that the ionization potential is a measure of the n donor ability and consequently the proton affinity of a base.[16] The computed results obtained in this study reflect this same type of correlation, provided that the n orbitals being compared are similar.[17] In a relevant study of protonated methylamines, Morokuma noted that while the electrostatic energy is the largest contributor to the proton affinities of these bases, it is the polarization energy which determines the specific order of proton affinity. Thus, he concluded that the methyl group makes an amine more polarizable, thereby giving it a higher proton affinity.[9] It is interesting to note, however, that his data also show that the monomer property which correlates with increasing proton affinity of methyl-substituted amines is the n orbital energy of the base. Thus it appears that the strength of the bond formed between the nitrogen atom and the proton is strongly influenced by the availability of the nitrogen lone pair.

From the data obtained from the 4-31G calculations in the study of protonated substituted carbonyl compounds, it was observed that the proton acceptor oxygen atoms experience an increase in negative charge in the ions.[10] Similarly, the proton acceptor nitrogen atoms in the protonated azabenzenes have larger negative charges than in the corresponding bases, as shown in Table II. The increased negative charge on these atoms occurs as a result of the polarization of the electron density of the base by the proton and accompanies electron density transfer from the base to the proton. In these ions, a correlation between increasing charge transfer and increasing ion stability is not found, as charge transfer to H^+ is least in protonated 1,2-diazine. It is interesting to note, however, that in a series of ions in which there is a greater variation in stability, increasing charge transfer tends to parallel increasing stability, as shown by the data in Table III for the protonation of NH_3, pyridine, and HCN.

The data in Table III for NH_3, pyridine, and HCN and their complexes with HF, H_2O, and H^+ may be used to compare the proton affinities and hydrogen bonding abilities of three distinctively different nitrogen bases. These data show that increasing stability of the hydrogen bonded complexes correlates with increasing p character of the nitrogen lone pair orbital,[18] and that a correlation does not exist between hydrogen bond

Table III. Properties of Nitrogen Bases and Their Complexes[a]

STO-3G Results			
	$B = NH_3$	$B = C_5H_5N$	$B = HCN$
$\Delta E(F\text{-}H\cdots B)$[b]	−8.3	−6.6	−3.6
$\Delta E(HOH\cdots B)$[b]	−5.9	−4.7	−2.6
$-\delta\Delta E(BH^+)$	−16.1	0.0	−71.1
$\epsilon(N1s)$	−416.7	−417.5	−418.6
$\epsilon(n)$	−9.75	−9.20	−13.41
$Q(N)$	7.440	7.241	7.161
$Q(H^+)$	0.635	0.680	0.564

4-31G Results			
	$B = NH_3$	$B = C_5H_5N$	$B = HCN$
$-\delta\Delta E(BH^+)$	−15.9	0.0	−58.7
$\epsilon(N1s)$	−422.3	−423.1	−424.2
$\epsilon(n)$	−11.44	−11.12	−15.57
$Q(N)$	7.879	7.556	7.344
$Q(H^+)$	0.503	0.526	0.429

Experimental Data			
	$B = NH_3$	$B = C_5H_5N$	$B = HCN$
$-\delta\Delta H(BH^+)$[c]	−15.8	0.0	−43.6
IP	10.15[d]	9.6[e]	13.9[d]

[a] See Table II for definitions. [b] Hydrogen bond energies in kcal/mol, from ref 13. [c] Data from ref 3 and 4. [d] First ionization potentials in eV, taken from G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1967. [e] In pyridine, the energies of n and π electron ionizations are similar. The 9.6 eV value is that assigned by R. Gleiter, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **55**, 255 (1972).

strengths and n orbital energies. However, the n orbital energies once again correlate with the relative proton affinities of NH_3, pyridine, and HCN.

Summary

The data obtained in this study support the following statements.

(1) With the 4-31G basis set, the computed proton affinities of pyridine and the diazines are in reasonable agreement with experimental gas-phase proton affinities, which are overestimated by about 10%. The relative order of proton affinity (pyridine > 1,2-diazine > 1,3-diazine > 1,4-diazine) determined experimentally is reproduced by the calculations.

(2) In particular series of nitrogen bases, increasing n orbital energy of the base correlates with increasing proton affinity, provided that the n orbitals are similar in nature.

(3) The structures of these protonated ions indicate that the bond formed between the proton and the proton-acceptor atom has the structural characteristics of a normal intramolecular covalent bond.

(4) The order of proton affinity for the bases HCN, pyridine, and NH_3 does not parallel the order of hydrogen bonding ability. In the hydrogen bonded complexes, increasing stability correlates with increasing p character of the nitrogen lone pair orbital. For the protonated ions, increasing stability correlates with increasing n orbital energy of the base.

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(14) Both zero-point and correlation energy corrections are also being neglected. While these corrections and a larger basis set are required to obtain better absolute agreement with experimental proton affinities, they do not appear to be critical when relative proton affinities of related bases are being compared.

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(17) Such a correlation cannot be extended to compare pyridine with the diazines since the nature of the n orbital changes. In the diazines, interaction between the two n orbitals on the two nitrogen atoms results in a destabilization of the higher energy n orbital, which is delocalized over both nitrogen atoms. In pyridine the n orbital is essentially localized at the single proton acceptor atom. A similar situation was also reported in ref 10 in the study of the protonated substituted carbonyl compounds, where it was observed that the n orbital energy of glyoxal does not reflect the relative proton affinity of this molecule. In a recent experimental study, Beauchamp noted that the n-electron ionization potential of $CH_2(CN)_2$ does not correlate with the relative proton affinity of this molecule in a series of substituted nitriles RCN; see R. H. Staley, J. E. Kleckner, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 2081 (1976).

(18) It is also important to note that all of the azabenzenes considered in this study form stronger hydrogen bonds than HCN but weaker hydrogen bonds than NH_3 whether HF or H_2O is the proton donor; see ref 13.