(35) Deutsch, E.; Cheung, N. K. V. *J. Org. Chem.* **1973,** *38,* 1123.
(36) Menger, F. M.; Singh, T. D.; Bayer, F. L. *J. Am. Chem. Soc.* **1976,** *98,* 5011.
(37) Joris, L.; Schleyer, P. v. R. *Tetrahedron* **1968,** *24,* 5991.
(38) Wolf, J. F.; Harsch, P. G.; Taft, R. W., Jr. *J. Am. Chem. Soc.* **1975,** *97,* 2904.
(39) Hopkins, H. P., Jr.; Ali, S. Z. *J. Am. Chem. Soc.* **1977,** *99,* 2069.
(40) Bernasconi, C. F.; Carré, D. J. *J. Am. Chem. Soc.* **1979,** *101,* 2707.

# Molecular Orbital Theory of the Hydrogen Bond. 21. 2-Monosubstituted Pyridines as Proton Acceptors

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**Abstract:** Ab initio SCF calculations with the STO-3G basis set have been performed to investigate substituent effects on the hydrogen bonding ability of 2-R-pyridines as proton-acceptor molecules, with the substituents including $CH_3$, $NH_2$, OH, F, $C_2H_3$, CHO, and CN. The equilibrium water-2-R-pyridine dimers generally have open structures stabilized by the formation of a linear hydrogen bond through the nitrogen lone pair of electrons, except for the water-2-aminopyridine dimer, which is cyclic, and the water-2-hydroxypyridine dimer, which has 2-hydroxypyridine as the proton donor. The relative orientation of the pyridine ring and the water molecule in an equilibrium dimer is determined by secondary substituent effects which include long-range interactions and the alignment of the dipole moment vectors of the proton-donor and proton-acceptor molecules. The hydrogen bonds in the water-2-R-pyridine dimers are weaker than in the water-pyridine dimer in all cases except the water-2-aminopyridine dimer. Primary substituent effects alter the electronic environment at the nitrogen, and are reflected in the n orbital energies of the pyridine bases. These energies are linearly related to the hydrogen-bond energies of a particular set of dimers in which the pyridine ring is perpendicular to the plane of the water molecule. Secondary substituent effects also influence the relative stabilities of the equilibrium water-2-R-pyridine dimers.

## Introduction

Recent developments in experimental methods for studying organic ion-molecule equilibria in the gas phase have provided valuable new data on the gas-phase basicities of molecules toward acids such as $H^+$ and $Li^+$.[1-4] A comparison of these data with basicities measured in solution has emphasized the mediating influence of the solvent on molecular basicity.[1,5-7] Paralleling these experimental developments and contributing to a better understanding of the factors which influence gas-phase and solution basicities has been the application of ab initio molecular orbital theory to the fundamental acid-base reactions of protonation, lithium ion complexation, and hydrogen-bond formation.[8-17]

An important series of organic compounds for which experimentally determined basicities in the gas phase and in aqueous solution are now available are the substituted pyridines.[6] The results of ab initio molecular orbital calculations of the association energies of some of these bases with $H^+$ and $H_2O$ have also been reported.[6,18-20] However, there has not yet been a thorough and systematic study to determine the equilibrium structures of these acid-base complexes, nor a detailed analysis of substituent effects on their structures and energies. Therefore, such an investigation has been initiated in this laboratory. The structures and stabilization energies of a set of hydrogen-bonded complexes containing HF or $H_2O$ as proton donors and pyridine or one of the diazines as proton acceptors have already been reported.[21,22] This investigation has now been extended to include another series of dimers which has water as the proton donor and a monosubstituted pyridine (2-R-pyridine) as the proton acceptor, with R including the isoelectronic saturated groups $CH_3$, $NH_2$, OH, and F and the unsaturated groups $C_2H_3$ (vinyl), CHO, and CN.

Owing to the particular geometry of the proton acceptor 2-R-pyridines and the structures of the water-2-R-pyridine complexes, particular rotations of the substituted pyridines are possible which leave the hydrogen bond intact, but which change the position of the substituent with respect to the water molecule. As a result, this series of dimers provides a unique opportunity to separately evaluate primary and secondary substituent effects on dimer structures and stabilities. The primary substituent effects are those which result from the influence of the substituent on the electronic environment at the nitrogen, and specifically on the availability of the nitrogen lone pair for hydrogen-bond formation. Secondary substituent effects arise from other long-range and dipole interactions which are due to the presence of the substituent in the 2 position of pyridine. The importance of such secondary substituent effects has long been recognized from the failure of the Hammett substituent constants for ortho-substituted aromatic rings to correlate with rate or equilibrium processes, presumably because ortho substituents are close enough to the reaction site to exert a significant proximity effect. The results of this present study may therefore provide a more detailed and quantitative insight into such ortho effects. The twofold aim of this investigation is to determine the equilibrium structures and stabilization energies of the water-2-R-pyridine dimers and to examine in detail primary and secondary substituent effects on these structures and stabilities.

## Method of Calculation

Wave functions for the closed-shell ground states of the monomers and the hydrogen-bonded complexes have been expressed as single Slater determinants $\Psi$

$$\Psi = |\psi_1(1)\bar{\psi}_1(2)\ldots\psi_n(2n-1)\bar{\psi}_n(2n)|/\sqrt{(2n)!}$$

consisting of a set of doubly occupied molecular orbitals. These orbitals $\psi_i$ are expressed as linear combinations of atomic basis functions $\phi_\mu$ (the LCAO approximation)

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

with the expansion coefficients $c_{\mu i}$ determined from the

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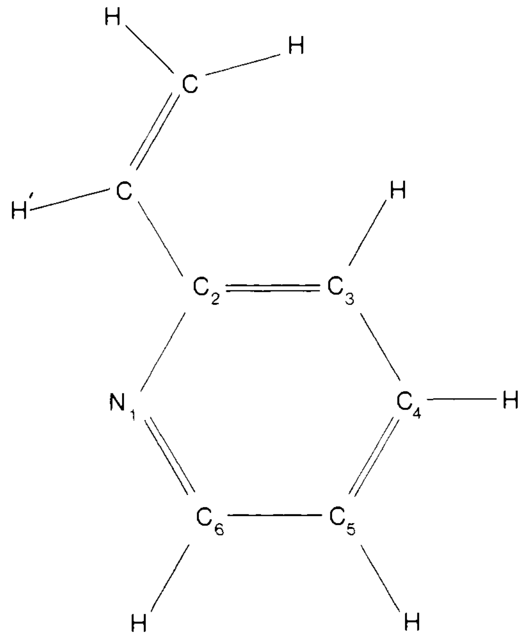

Figure 1. 2-Vinylpyridine with C-H' s-cis to $N_1$-$C_2$.

**Table I.** Structures and Energies of Water-2-R-Pyridine Dimers in Set A[a]

| R | $\theta_1'$[b] | $\chi_1$ | $\theta_2$ | $\chi_2$ | $\phi$ | $R$ | $\Delta E$[c] |
|---|---|---|---|---|---|---|---|
| H[d] | −2 | 0 | 175 | 0 | 180 | 2.97 | −0.007 25 |
| $CH_3$ | 0 | 0 | 169 | 0 | 180 | 2.97 | −0.006 96 |
| $NH_2$ | 0 | 0 | 168 | 0 | 180 | 2.95 | −0.006 89 |
| OH | 1 | 0 | 165 | 0 | 180 | 3.00 | −0.005 10 |
| F[e] | −3 | 0 | 178 | 0 | 180 | 3.00 | −0.006 98 |
| $C_2H_3$ | 0 | 0 | 168 | 0 | 180 | 2.99 | −0.006 61 |
| CHO | 0 | 0 | 168 | 0 | 180 | 3.01 | −0.005 86 |
| CN[e] | −2 | 0 | 175 | 0 | 180 | 3.05 | −0.005 94 |

[a] Angles in degrees, $R$(O-$N_1$) in ångstroms. [b] $\theta_1' = \theta_1 - 50°$. $\theta_1' = 0°$ indicates a linear O-H···$N_1$ hydrogen bond. [c] $\Delta E$ is the intermolecular energy in au. [d] Data from ref 21. [e] Equilibrium structure.

Roothaan equations.[23] The minimal STO-3G basis set with standard scale factors[24] has been employed for the LCAO expansions.

The equilibrium $C_s$ structures and the properties of the 2-R-pyridines have already been reported.[25] In these molecules, an in-plane hydrogen atom (H') bonded to X (X is the first-row atom of the substituent bonded to $C_2$) is oriented so that X-H' is s-cis to $N_1$-$C_2$, as illustrated in Figure 1 for 2-vinylpyridine. With the optimized geometries of the 2-R-pyridines and of water held rigid,[26] three sets of hydrogen-bonded structures (A, B, and C) have been investigated. These dimer structures are readily described in the standard intermolecular coordinate system used previously,[21,22] which consists of an intermolecular distance (the O-$N_1$ distance in these complexes) and five intermolecular angles which are defined with reference to the principal axes of the proton-donor and proton-acceptor molecules and the intermolecular line, as shown in Figures 2 and 3.[27] The water-2-R-pyridine dimers in set A have $C_s$ symmetry, and are those in which the substituent is cis to the external non-hydrogen-bonded hydrogen ($H_e$) of water with respect to the intermolecular O-$N_1$ line, as shown in Figure 2. Dimers in set C, illustrated in Figure 3, also have $C_s$ symmetry, but have the R group trans to $H_e$. Dimers in both sets A and C have been optimized under the constraint of $C_s$ symmetry to ±0.01 Å in the intermolecular O-$N_1$ distance and to ±1° (where possible) in each intermolecular angle. Dimers in set B are asymmetric, and have not been geometry optimized. In set B dimers, the symmetry plane of the substituted pyridine has been constrained to be perpendicular to the plane of the water molecule, and the proton-donor and proton-acceptor molecules have been ori[illegible] so that the O-H bond of water and the principal axis of [illegible]oton-acceptor molecule are collinear with the intermolecular line.[28] The A, B, and C structures are most easily related through rotation of the substituted pyridine about its principal axis, and are separated by 90° along this, the $\chi_2$ rotational coordinate. For dimers in sets A, B, and C, the intermolecular (hydrogen bond) energy is computed as the difference between the total dimer energy and the sum of the energies of the optimized monomers. All calculations have been performed in double precision on an IBM 370/148 computer.

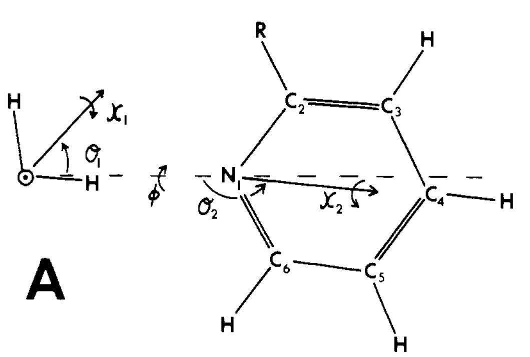

Figure 2. The water-2-R-pyridine cis dimer A showing principal axes and intermolecular coordinates.

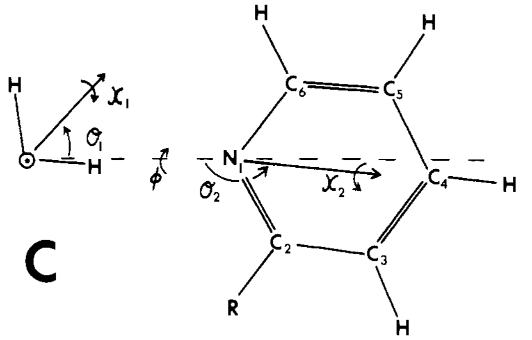

Figure 3. The water-2-R-pyridine trans dimer C showing principal axes and intermolecular coordinates.

## Results and Discussion

**Structures.** The ab initio calculations carried out in this study show that the water-2-R-pyridine dimers may have cis (A), perpendicular (B), or trans (C) equilibrium structures, depending on the nature of the substituent. The water-2-fluoropyridine and water-2-cyanopyridine dimers have equilibrium open cis structures. The water-2-pyridinecarboxaldehyde dimer has an open trans structure, while the water-2-aminopyridine dimer has a cyclic trans structure. Both the water-2-methylpyridine and water-2-vinylpyridine dimers have the open perpendicular structure of the water-pyridine dimer.[21] No equilibrium water-2-hydroxypyridine dimer which has 2-hydroxypyridine as the proton-acceptor molecule through the nitrogen lone pair exists on the intermolecular surface. Some of the structural features of the water-2-R-pyridine dimers in sets A, B, and C will now be considered in detail.

The optimized structures of dimers in set A are reported in Table I, along with the structure of the optimized water-pyridine dimer with planar $C_s$ symmetry.[21] As indicated in Table I, only the dimers with 2-fluoropyridine and 2-cyanopyridine as proton acceptors have equilibrium cis structures. The

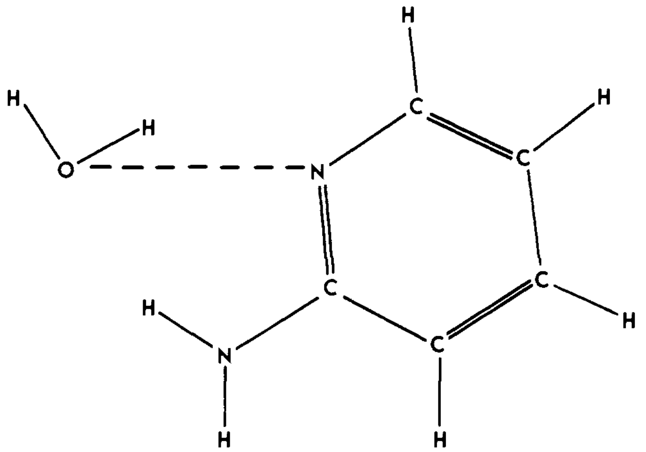

Figure 4. The structure of the water-2-aminopyridine dimer C.

**Table II.** Structures and Energies of Water-2-R-Pyridine Dimers in Set C[a]

| R | $\theta_1'$ | $\chi_1$ | $\theta_2$ | $\chi_2$[b] | $\phi$[b] | $R$ | $\Delta E$ |
|---|---|---|---|---|---|---|---|
| H | −2 | 0 | 175 | 180 | 180 | 2.97 | −0.007 25 |
| $CH_3$ | −3 | 0 | 178 | 0 | 0 | 2.97 | −0.007 15 |
| $NH_2$[c] | 28 | 0 | 154 | 180 | 180 | 2.84 | −0.010 22 |
| OH | | | | | | | |
| F | −5 | 0 | 177 | 180 | 180 | 3.01 | −0.006 29 |
| $C_2H_3$ | −2 | 0 | 177 | 0 | 0 | 2.98 | −0.006 75 |
| CHO[c] | 0 | 0 | 180 | 180 | 180 | 3.00 | −0.006 17 |
| CN | −8 | 0 | 176 | 0 | 0 | 3.06 | −0.004 45 |

[a] See footnotes *a*-*d*, Table I. [b] The combination $\chi_2 = \phi = 0°$ with $\theta_2 < 180°$ places the principal axes of the proton-donor and proton-acceptor molecules cis with respect to the O-$N_1$ line. The combination $\chi_2 = \phi = 180°$ with $\theta_2 < 180°$ gives a trans arrangement of principal axes. [c] Equilibrium structure.

**Table III.** Intermolecular Energies (kcal/mol) of Water-2-R-Pyridine Dimers in Sets A, B, and C[a]

| R | A | B | C |
|---|---|---|---|
| H | 4.5 | $\underline{4.6}$[b] | 4.5 |
| $CH_3$ | 4.4 | $\underline{4.5}$ | 4.5 |
| $NH_2$ | 4.3 | 5.0 | $\underline{6.4}$ |
| OH | 3.2 | 3.8 | — |
| F | $\underline{4.4}$ | 4.1 | 3.9 |
| $C_2H_3$ | 4.1 | $\underline{4.3}$ | 4.2 |
| CHO | 3.7 | 3.9 | $\underline{3.9}$ |
| CN | $\underline{3.7}$ | 3.0 | $\underline{2.8}$ |

[a] Energy of the most stable structure is underlined. [b] The fully optimized water-pyridine B dimer has a stabilization energy of 4.7 kcal/mol. See ref 21.

preference for cis structures may be attributed to stabilizing long-range interactions between the substituents F and CN and the external non-hydrogen-bonded hydrogen ($H_e$) of water and to a favorable orientation of the dipole moment vectors of the hydrogen-bonded pair. In each of these dimers, a directed lone pair of electrons on the pyridine nitrogen $N_1$ takes part in the formation of an essentially linear hydrogen bond. Thus, the structures of the water-2-fluoropyridine and water-2-cyanopyridine dimers are in agreement with the idealized structure of the general hybridization model (GHM) for an open hydrogen-bonded complex.[29]

The optimized but nonequilibrium structures of the remaining water-2-R-pyridine dimers in set A deviate somewhat from the idealized GHM structure, especially in the orientation of the proton-acceptor molecules. In these dimers, the interaction between the substituent and $H_e$ is unfavorable, causing the proton-acceptor molecule to rotate (in the direction of decreasing $\theta_2$) in order to increase the distance between the substituent and $H_e$. By comparison, the repulsion between $H_e$ and the hydrogen atom bonded to $C_2$ in the water-pyridine dimer is much weaker. As a result, the optimized structure of the water-pyridine dimer in set A is similar to the equilibrium structures of the water-2-fluoropyridine and water-2-cyanopyridine dimers, even though it is not an equilibrium structure on the intermolecular surface.

The optimized structures of dimers in set C in which the substituent is trans to the external hydrogen atom of water are reported in Table II. Trans structures are equilibrium structures for the water-2-aminopyridine and water-2-pyridinecarboxaldehyde dimers. However, it is evident from the data of Table II that the structures of these two dimers are quite different. While the structure of the water-2-pyridinecarboxaldehyde dimer is consistent with the idealized GHM structure, the water-2-aminopyridine dimer lacks both a directed lone pair of electrons (the angle $\theta_2$ is 154° instead of approximately 180°) and a linear hydrogen bond (the angle between the O-H bond and the intermolecular line is 28°). The equilibrium water-2-aminopyridine dimer is cyclic, as shown in Figure 4, and is stabilized by two distorted O-H···$N_1$ and N-H···O hydrogen bonds and by a favorable alignment of the dipole moment vectors of water and 2-aminopyridine. The structure of this dimer is similar to the equilibrium structures of the water-formamide and water-urea dimers which are also cyclic when the water molecule and the $NH_2$ group are cis with respect to the carbonyl C-O bond.[30] While the water-2-aminopyridine dimer shown in Figure 4 is an equilibrium structure with respect to changes along each intermolecular coordinate, it has not been established whether this dimer is a stable structure or represents a saddle point on the intermolecular surface, which could be converted to a dimer having 2-aminopyridine as the single proton-donor molecule and water as the proton acceptor.

It is apparent from the structure of the water-2-aminopyridine dimer C that the presence of an acidic hydrogen in the substituent s-cis to $N_1$-$C_2$ can result in the formation of a second hydrogen bond in which the substituent is the proton donor. In the case of the water-2-hydroxypyridine complex, the OH group is such a strong proton donor that the path of increasing stability on the intermolecular surface leads directly to a dimer in which 2-hydroxpyridine is the proton-donor molecule.[31] Since the optimized cis structure of the water-2-hydroxypyridine dimer is also a nonequilibrium structure which is converted to a trans structure without a $\chi_2$ rotational barrier, there is no equilibrium dimer on this surface which has 2-hydroxypyridine as the proton-acceptor molecule when the O-H bond of 2-hydroxypyridine is s-cis to $N_1$-$C_2$.

The remaining water-2-R-pyridine dimers, water-2-methylpyridine and water-2-vinylpyridine, have neither cis (A) nor trans (C) structures, but equilibrium B structures similar to the water-pyridine dimer. The B structures are favored since the repulsive long-range interactions which tend to destabilize the planar A and C structures are minimized in the perpendicular structures. The orientation of the dipole moment vectors does not influence the equilibrium structures of these dimers, since the dipole moment vectors of 2-methylpyridine and 2-vinylpyridine are nearly collinear with the principal axes. Although the B structures are favored, it should be recognized that, because long-range interactions are weak and the dipole interactions do not vary significantly as the proton-acceptor molecules rotate about their principal axes, there is essentially free rotation of these molecules in the water-2-methylpyridine and water-2-vinylpyridine dimers.

**Energies.** The data of Table III indicate that the hydrogen bonds in the water-2-R-pyridine dimers are weaker than in the water-pyridine dimer in all cases except the water-2-aminopyridine dimer. The relative stabilities of the equilibrium dimers in this series are determined by both primary and secondary substituent effects, which may be separately evaluated by analyzing the stabilization energies of the perpendicular (B) and the planar (A and C) dimers. As noted above, these dimers are related on the intermolecular surface through rotation of the substituted pyridine about its principal axis (the $\chi_2$ rotation). Since the nitrogen lone pair lies on this axis, this rotation leaves the hydrogen bond intact. Thus, the primary electronic effects of the substituents which influence the availability of the nitrogen lone pair for hydrogen bonding will not be affected by this rotation, and can be readily evaluated from the energies of the perpendicular B dimers. On the other hand, the $\chi_2$ rotation does affect secondary substituent effects, since these include long-range interactions between the substituent and the proton-donor molecule, and the relative orientation of the dipole moment vectors of the hydrogen-bonded pair. Secondary substituent effects may therefore be evaluated from the energies of the planar A and C dimers relative to B. These primary and secondary substituent effects on the stabilities of the water-2-R-pyridine dimers will now be considered in detail.

As evident from the data of Table III for the perpendicular structures, the hydrogen-bond energies of the water-2-R-pyridine B dimers vary by 2.0 kcal/mol in this series. This variation is a direct consequence of the primary electronic effects of the substituents on the pyridine nitrogen. As noted previously,[25] the substituents $CH_3$, $NH_2$, OH, F, and $C_2H_3$ are $\pi$ electron donating and $\sigma$ electron withdrawing groups relative to H, and these $\pi$ and $\sigma$ effects have opposing effects on the hydrogen-bonding ability of the pyridine nitrogen. Through $\pi$ donation, the substituents increase the $\pi$ electron density at the nitrogen. This tends to destabilize the n orbital, making the nitrogen lone pair more available for hydrogen bonding. On the other hand, $\sigma$ withdrawal decreases the nitrogen electron density and stabilizes the n orbital, thereby tending to decrease the hydrogen-bonding ability of the nitrogen. The data for the set B dimers indicate that, except for $NH_2$, which is the strongest $\pi$ electron donating group, the $\sigma$ withdrawing effect of these substituents dominates and leads to a weakening of the hydrogen bond. Substitution of CHO and CN, which withdraw both $\sigma$ and $\pi$ electron density, also leads to a weakening of the hydrogen bonds in the water-2-pyridinecarboxaldehyde and water-2-cyanopyridine dimers. Substitution of CN, which is the strongest electron-withdrawing group, leads to a significant weakening of the hydrogen bond in the water-2-cyanopyridine B dimer by 1.6 kcal/mol relative to the water-pyridine dimer.

A linear relationship has been found between the n orbital energies of the substituted pyridines[25] and the hydrogen-bond energies of the water-2-R-pyridine dimers in set B, as shown in Figure 5. A least-squares fit yielded the equation

$$\Delta E = 1.72\epsilon_n + 20.36$$

(where $\Delta E$ is the hydrogen-bond energy in kcal/mol, and $\epsilon_n$ is the n orbital energy in eV), with a correlation coefficient of 0.97.[32] This correlation demonstrates that the presence of the substituent in the 2 position of pyridine influences the hydrogen-bonding ability of these bases through changes in the electronic environment at the nitrogen which alter the availability of the nitrogen lone pair and are reflected in the n orbital energies. While the n orbital energy has often been assumed to be an indicator of base strength for hydrogen bonding, it has not been possible previously to establish a linear relationship between n orbital energies and hydrogen-bond energies in a closely related series of dimers partly because of the difficulty of separating primary and secondary substituent effects. In the water-2-R-pyridine B dimers where primary substituent effects are essentially isolated in the perpendicular structures, such a linear relationship is clearly demonstrated.[33]

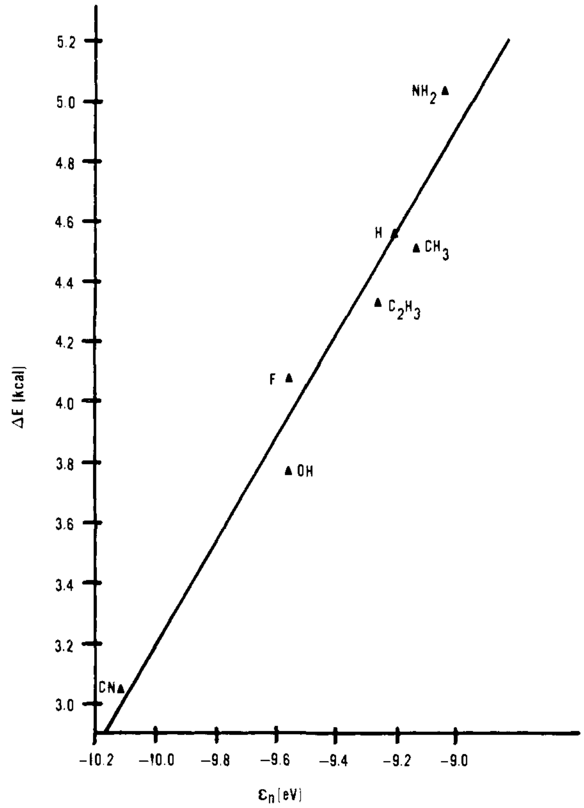

**Figure 5.** The n orbital energies of the 2-R-pyridines vs. the hydrogen-bond energies of the water-2-R-pyridine B dimers.

The secondary effects of substituents on the hydrogen-bonding ability of the 2-R-pyridines may now be evaluated by comparing the stabilities of the optimized A and C structures with the corresponding B structure. As noted above, cis structures are equilibrium structures for the water-2-fluoropyridine and water-2-cyanopyridine dimers. These are stabilized by a favorable alignment of dipole moment vectors and by an attractive interaction between the substituent F or CN and the external hydrogen of water. The importance of these secondary interactions is evident from the data of Table III, which show that 2-fluoropyridine is a slightly stronger base toward water than 2-vinylpyridine, even though primary substituent effects favor 2-vinylpyridine as the stronger base. Similarly, although 2-cyanopyridine should be a significantly weaker base than any other substituted pyridine as a result of the strong electron-withdrawing ability of the CN group, secondary effects make 2-cyanopyridine competitive with 2-pyridinecarboxaldehyde as a base for hydrogen bonding with water.

Although the dipole alignments in the water-2-hydroxypyridine and water-2-pyridinecarboxaldehyde dimers are also favorable in the cis (A) structures, these are not equilibrium structures on the respective intermolecular surfaces due to repulsive interactions between $H_e$ and H′. Rotation of 2-pyridinecarboxaldehyde about its principal axis relieves this repulsion, but leads to a more unfavorable dipole alignment in the trans structure of the dimer. As a result, the potential surface along the $\chi_2$ curve is flat, with a rotational barrier of only 0.2 kcal/mol measured from the preferred dimer C. Similarly, rotation of 2-hydroxpyridine about its principal axis stabilizes the water-2-hydroxypyridine complex by removing the very acidic proton H′ from proximity to $H_e$ in dimer A. Rotation by 180° produces a trans dimer C, which, when fully optimized, has 2-hydroxypyridine as the proton donor.

**Table IV.** Electron Population Changes in Water–2-R-Pyridine Dimers[a]

| R | | O[b] | H[b] | $N_1$[b] | pyridine ring | change transfer to $H_2O$ |
|---|---|---|---|---|---|---|
| $CH_3$ | A | 0.040 | −0.035 | 0.014 | −0.027 | 0.030 |
| | C | 0.042 | −0.035 | 0.013 | −0.020 | 0.031 |
| $NH_2$ | A | 0.041 | −0.037 | 0.013 | −0.029 | 0.033 |
| | C | 0.043 | −0.047 | 0.017 | 0.010 | 0.002 |
| OH | A | 0.034 | −0.029 | 0.013 | −0.027 | 0.028 |
| F | A | 0.038 | −0.032 | 0.013 | −0.026 | 0.027 |
| | C | 0.035 | −0.032 | 0.013 | −0.020 | 0.026 |
| $C_2H_3$ | A | 0.038 | −0.033 | 0.014 | −0.024 | 0.028 |
| | C | 0.041 | −0.034 | 0.014 | −0.018 | 0.031 |
| CHO | A | 0.035 | −0.030 | 0.014 | −0.024 | 0.026 |
| | C | 0.038 | −0.031 | 0.013 | −0.016 | 0.028 |
| CN | A | 0.034 | −0.026 | 0.013 | −0.021 | 0.023 |
| | C | 0.028 | −0.027 | 0.013 | −0.012 | 0.021 |

[a] A negative value indicates a loss of electron density. [b] Atoms which are hydrogen bonded as O–H···$N_1$.

**Table V.** $\pi$ Electron Population Changes in Water–2-R-Pyridine Dimers[a]

| R | | $N_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | pyridine ring |
|---|---|---|---|---|---|---|---|---|
| $CH_3$ | A | 0.030 | −0.006 | 0.001 | −0.010 | −0.001 | −0.011 | 0.003 |
| | C | 0.030 | −0.012 | −0.001 | −0.010 | 0.000 | −0.006 | 0.001 |
| $NH_2$ | A | 0.031 | −0.005 | 0.000 | −0.010 | −0.003 | −0.011 | 0.002 |
| | C | 0.033 | −0.015 | 0.003 | −0.008 | 0.008 | −0.004 | 0.017 |
| OH | A | 0.027 | −0.004 | 0.000 | −0.009 | −0.003 | −0.010 | 0.001 |
| F | A | 0.027 | −0.004 | −0.001 | −0.010 | −0.002 | −0.010 | 0.000 |
| | C | 0.027 | −0.008 | −0.002 | −0.010 | −0.001 | −0.005 | 0.001 |
| $C_2H_3$ | A | 0.029 | −0.007 | 0.001 | −0.009 | −0.001 | −0.011 | 0.002 |
| | C | 0.031 | −0.012 | 0.000 | −0.010 | 0.001 | −0.006 | 0.004 |
| CHO | A | 0.028 | −0.004 | 0.000 | −0.010 | −0.002 | −0.011 | 0.001 |
| | C | 0.029 | −0.010 | −0.001 | −0.010 | 0.001 | −0.006 | 0.003 |
| CN | A | 0.025 | −0.004 | −0.001 | −0.008 | −0.001 | −0.010 | 0.001 |
| | C | 0.024 | −0.008 | −0.002 | −0.009 | 0.000 | −0.009 | 0.001 |

[a] See footnote *a*, Table IV.

The presence of the strongest $\pi$ electron donating group $NH_2$ strengthens the hydrogen bond in the water–2-aminopyridine B dimer by 0.4 kcal/mol relative to the water–pyridine dimer. However, the equilibrium trans structure of this dimer is 1.4 kcal/mol more stable than B, owing to the formation of an N–H···O hydrogen bond and a favorable alignment of molecular dipole moment vectors. Secondary effects are also responsible for the destabilization of the water–2-aminopyridine A dimer by 0.7 kcal/mol relative to B. It is apparent from these data that secondary substituent effects have a significantly greater influence on the stability of the water–2-aminopyridine dimer than do the primary electronic effects of the strong $\pi$ donating substituent $NH_2$.

The nonpolar substituents $CH_3$ and $C_2H_3$ are very weak $\pi$ donating and $\sigma$ withdrawing groups. Since their presence has a relatively small effect on the electronic environment at the nitrogen, the hydrogen-bond energies of the perpendicular water–2-methylpyridine and water–2-vinylpyridine dimers are similar to that of the water–pyridine dimer. Secondary substituent effects are also small in these dimers, as reflected by the similar stabilities of corresponding A, B, and C structures. The dipole moment vectors of 2-methylpyridine and 2-vinylpyridine are nearly coincident with the principal axes, so that rotation of these molecules about their principal axes produces only small changes in the alignment of dipole moment vectors in the A, B, and C structures. The interactions between $H_e$ and H′ in the cis structure and $H_e$ and $H_6$ in the trans (see Figure 3) are repulsive but small, and are minimized in the equilibrium perpendicular structures. The absence of strong secondary effects is responsible for flat $\chi_2$ potential curves on the water–2-methylpyridine and water–2-vinylpyridine intermolecular surfaces.

**Electron Populations.** It is well known that hydrogen-bond formation leads to changes in atomic electron populations. In the water–2-R-pyridine dimers, the electron redistribution which accompanies dimer formation is evident from the dipole moments of the hydrogen-bonded complexes, which are greater than the vector sums of the monomer dipole moments, and from the Mulliken population data[34] which are shown in Tables IV and V. Hydrogen bonding leads to characteristic increases in the electron densities of the oxygen and nitrogen atoms and to a decrease in the electron density of the hydrogen atom which form the O–H···$N_1$ hydrogen bond. It is also accompanied by charge transfer from the proton-acceptor molecule to the proton donor. In the open dimers, the amount of electron density transferred varies from 0.021 e in the water–2-cyanopyridine dimer A to 0.033 e in the water–2-aminopyridine dimer A. By contrast, only 0.002 e is transferred to the water molecule in the cyclic water–2-aminopyridine dimer C. In the A dimers, electron transfer from the proton-acceptor molecule occurs almost exclusively from the pyridine ring. In the C structures, electron density is lost primarily by the ring but also by the substituent. Hydrogen bond formation leaves the total $\pi$ electron density of the pyridine ring essentially unchanged in the open structures, but it does produce a redistribution of $\pi$ electrons which increases the $\pi$ density of $N_1$ and decreases the $\pi$ electron densities of $C_2$, $C_4$, and $C_6$. This reinforces the changes which occur in the $\pi$ system when the nitrogen atom is introduced into the benzene ring.

## Conclusions

The following points summarize the principal results of the ab initio calculations performed in this study of the water–2-R-pyridine dimers.

(1) Except for the water–2-aminopyridine dimer, which has a trans cyclic structure, and the water–2-hydroxypyridine dimer, which has 2-hydroxypyridine as the proton-donor molecule, the water–2-R-pyridine dimers have open structures in which an essentially linear hydrogen bond is formed through the $\sigma$ lone pair of electrons on the pyridine nitrogen. The water–2-fluoropyridine and water–2-cyanopyridine dimers have equilibrium cis structures, the water–2-pyridinecarboxaldehyde dimer has an equilibrium trans structure, and the water–2-methylpyridine and water–2-vinylpyridine dimers have perpendicular equilibrium structures similar to the water–pyridine dimer. Whether the equilibrium structure of a water–2-R-pyridine dimer is cis, trans, or perpendicular is determined by secondary substituent effects which include the orientation of the dipole moment vectors of the proton-donor and proton-acceptor molecules and long-range interactions between the substituent and the water molecule.

(2) The hydrogen bonds in the water–2-R-pyridine dimers are weaker than in the water–pyridine dimer in all cases except the water–2-aminopyridine dimer. The weakening of the hydrogen bonds in these dimers is a result of the $\sigma$ electron withdrawing effects of the substituents.

(3) The relative stabilities of the perpendicular water–2-R-pyridine dimers are determined by the primary effects of the substituents on the electronic environment at the nitrogen, which are reflected in the n orbital energies of the pyridine bases. A linear correlation exists between these n orbital energies and the hydrogen-bond energies of the perpendicular water–2-R-pyridine dimers. Secondary substituent effects are also important in determining the relative stabilities of the equilibrium water–2-R-pyridine dimers.

(4) Hydrogen-bond formation in open water-2-R-pyridine dimers leads to charge transfer from the substituted pyridine molecule to the water molecule, to characteristic changes in the electron densities of the O, H, and $N_1$ atoms which form the O-H···$N_1$ hydrogen bond, and to a redistribution of the $\pi$ electron density of the pyridine ring.

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## References and Notes

(1) R. W. Taft in "Proton-Transfer Reactions", E. F. Caldin and V. Gold, Eds., Wiley, New York, 1975, pp 31–77; E. M. Arnett, *ibid.*, pp 79–101.
(2) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98,** 311 (1976).
(3) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99,** 5417 (1977).
(4) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97,** 5920 (1975).
(5) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98,** 318 (1976).
(6) E. M. Arnett, B. Chawla, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **99,** 5729 (1977).
(7) W. R. Davidson, J. Sunner, and P. Kebarle, *J. Am. Chem. Soc.*, **101,** 1675 (1979).
(8) A. C. Hopkinson and I. G. Csizmadia, *Can. J. Chem.*, **52,** 546 (1974).
(9) L. Radom, *Aust. J. Chem.*, **28,** 1 (1975).
(10) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98,** 4400 (1976).
(11) A. Pullman and P. Brochen, *Chem. Phys. Lett.*, **34,** 7 (1975).
(12) P. A. Kollman and S. Rothenberg, *J. Am. Chem. Soc.*, **99,** 1333 (1977).
(13) J. E. Del Bene, *J. Am. Chem. Soc.*, **100,** 1673 (1978).
(14) J. E. Del Bene and S. Radovick, *J. Am. Chem. Soc.*, **100,** 6936 (1978).
(15) J. E. Del Bene, *Chem. Phys.*, **40,** 329 (1979).
(16) J. E. Del Bene, *Chem. Phys. Lett.*, **64,** 227 (1979).
(17) P. A. Kollman in "Applications of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press, New York, 1977, pp 109–152.
(18) I. G. John, G. L. D. Ritchie, and L. Radom, *J. Chem. Soc., Perkin Trans. 2,* 1601 (1977).
(19) W. F. Reynolds, P. G. Mezey, W. J. Hehre, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, **99,** 5821 (1977).
(20) J. E. Del Bene, *J. Am. Chem. Soc.*, **99,** 3617 (1977).
(21) J. E. Del Bene, *J. Am. Chem. Soc.*, **97,** 5330 (1975).
(22) J. E. Del Bene, *Chem. Phys.*, **15,** 463 (1976).
(23) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23,** 69 (1951).
(24) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51,** 2657 (1969).
(25) J. E. Del Bene, *J. Am. Chem. Soc.*, in press.
(26) J. E. Del Bene, *J. Chem. Phys.*, **62,** 1961 (1975).
(27) For water, the principal axis is the $C_2$ symmetry axis, with origin at the oxygen, while the principal axis of a substituted pyridine is the bisector of the $C_6$–$N_1$–$C_2$ angle, with origin at the nitrogen. The angle $\theta_1$ is the angle between the principal axis of water and the intermolecular line, while $\chi_1$ is the angle of rotation of the water molecule about its principal axis. The angles $\theta_2$ and $\chi_2$ are defined analogously for the proton-acceptor molecule. The fifth angle $\phi$ measures rotation of the principal axis of the proton-acceptor molecule about the intermolecular line.
(28) The B dimers are described by the angular coordinates $\theta_1 = 50$, $\theta_2 = 180$, $\chi_1 = \phi = 0$, and $\chi_2 = 90°$. The O–$N_1$ distance is that found in the corresponding more stable A or C structure except for the water–2-aminopyridine dimer, where R is the distance in the A structure.
(29) J. E. Del Bene, *J. Am. Chem. Soc.*, **100,** 1387 (1978).
(30) J. E. Del Bene, *J. Chem. Phys.*, **62,** 1314 (1975); **63,** 4666 (1975).
(31) This dimer is further stabilized when the water molecule bends out of the dimer symmetry plane to direct one of the oxygen lone pairs toward the OH group.
(32) The data for the water–2-pyridinecarboxaldehyde dimer have been omitted, since the n orbital in 2-pyridinecarboxaldehyde is highly delocalized over the pyridine nitrogen and the carbonyl oxygen, and is not a suitable measure of the electronic environment at the nitrogen.
(33) Previous studies have shown that a correlation exists between the n orbital energies and the proton affinities of a series of bases, provided that the n orbitals are similar. For example, see ref 20 and R. H. Staley, J. E. Kleckner, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98,** 2081 (1976).
(34) R. S. Mulliken, *J. Chem. Phys.*, **23,** 1833 (1955).

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# Proton Affinities of Ethylidenimine and Vinylamine

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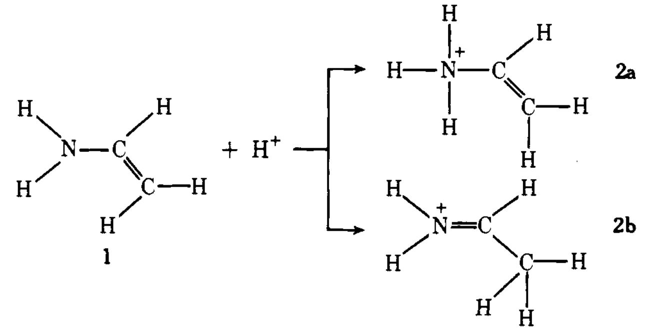
**Abstract:** The proton affinity of ethylidenimine has been determined by ion cyclotron resonance to be 213.2 ± 2 kcal/mol relative to the value for $NH_3$ of 203.6 kcal/mol. This value is combined with the known heat of formation of the protonated species to give a value of 2 ± 4 kcal/mol for the heat of formation (298 K) of the neutral imine. The proton affinity for C-protonation of vinylamine was calculated using ab initio molecular orbital theory with a DZ + D basis set to be 7.0 kcal/mol higher than that of the imine, giving 220.2 kcal/mol. The proton affinity for N-protonation of vinylamine was calculated to be 18.7 kcal/mol lower than that for C-protonation. The calculated proton affinities for ammonia, methylamine, dimethylamine, and trimethylamine using the same basis set are also given.

The determination of molecular proton affinities can yield valuable insight into both solution and gas-phase properties.[1] Work to date has concentrated on common functional groups, in particular, the proton affinities of amines.[2] We have begun to look at the gas-phase ion chemistry of some more unusual functional groups, including enamines and imines, and report here some initial ion cyclotron resonance (ICR) studies and ab initio calculations in this area.

Enamines are a classic example of an ambident reagent showing reactivity at both C and N with electrophilic species. This property is illustrated below for the reaction of a proton with the simplest enamine, vinylamine (**1**). Interestingly enough, in solution, for both protonation and the synthetically important alkylation reactions, the enammonium ion (e.g., **2a**)



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