of the pore, at which the rotational motion of the solute molecule is drastically restricted, may be in the range from 25 to 50 times the volume of solute molecule. In the smaller pore, the interaction of solute molecule with the surrounding molecules, that is, solvent or polymer lattice, works more easily and the anisotropy of the interaction becomes larger ($\kappa \rightarrow$ larger), and consequently the anisotropy of rotational diffusion also becomes larger ($N \rightarrow$ larger).

All those results cited above suggest that the rotational diffusion is mainly determined by the size of the solute molecule, i.e., by the physical nature of the latter. However, the data of the present investigation also suggest that the chemical effects also affect the rotational diffusion of the solute molecules by reducing the rate of the rotational motion. In this investigation, nothing was learned about translational diffusion of the solute molecule in PVA gel. However, the translational motion of the solute molecule in PVA gels seems to be inhibited by the chain of PVA gels compared to the bulk solution.

In the present paper, the analysis of line width is carried out by the model of axially symmetric rotational diffusion. Actually, one hyperfine line due to N nucleus is composed of 13 hyperfine structures due to H nuclei, which results in inhomogeneous broadening. In the case of Tempone radical, the hyperfine coupling constant due to H nuclei is very small compared with that in the other radicals I, II, IV, and V, and the effect of inhomogeneous broadening is not considered in the discussion. It is reasonably said, however, that the conclusion obtained in this experiment shows the correct trend of rotational motion in the limited pore. In the case of Tempo radical, which has a larger hyperfine coupling due to H nuclei, similar analysis without an inhomogeneous broadening fails to explain the line width. The analysis of line width for Tempo radical in PVA gels will be discussed separately.

It has been recently noticed[19] that the confinement of water molecules in a small space of polyacrylamide is effective for the promotion of freezing. These phenomena might have relevance to the motion of molecules in limited space.

Acknowledgments. The authors wish to thank Dr. S. H. Koenig of IBM Laboratory for discussion on the critical volumes and Dr. M. Yoshida of the University of Tokyo for synthesizing nitroxide radicals used and for discussing their chemical nature.

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Molecular Orbital Theory of the Hydrogen Bond. 22. 4-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 4-R-pyridine bases, with R including the substituents CH_3, NH_2, OH, F, C_2H_3, CHO, and CN. The equilibrium structures of the water–4-R-pyridine dimers are stabilized by a linear hydrogen bond formed through the nitrogen lone pair of electrons, and are similar to the equilibrium structure of the water–pyridine dimer with the plane of the pyridine ring perpendicular to that of the water molecule, with little variation in intermolecular distances. Except for F, substitution of a π donating and σ withdrawing group for H in the 4 position strengthens the hydrogen bond in water–4-R-pyridine dimers, while substitution of a σ and π electron-withdrawing group weakens the hydrogen bond. Primary substituent effects alter the electronic environment at the pyridine nitrogen, and are evident from changes in n-orbital energies upon substitution. These n-orbital energies are linearly related to the hydrogen-bond energies of the water–4-R-pyridine dimers provided that the n orbital is essentially localized at the nitrogen. A comparison of the stabilities of corresponding perpendicular water–2-R-pyridine and water–4-R-pyridine dimers shows that the hydrogen bond in the latter is stronger. However, secondary substitutent effects may further stabilize planar equilibrium structures of particular water–2-R-pyridine dimers to the extent that the 2-R-pyridine may form the more stable complex.

Introduction

Substituent effects on base properties are a major factor determining the behavior of compounds in important chemical and biochemical processes, and have therefore been a subject of interest and investigation in modern chemistry. This interest has intensified recently, owing to developments in chemical ionization mass spectrometry and ion cyclotron resonance spectroscopy which now permit measurements of gas-phase ion-molecule equilibria and the energetics of ion-transfer reactions in the gas phase,[1–4] and by the application of ab initio molecular orbital theory to the study of isodesmic processes.[5] Combined theoretical and experimental data have led to new insights into substituent effects on molecular basicity, and comparisons with solution data have demonstrated the important role which the solvent may play in moderating basicity in condensed media.[6–9]

As part of a continuing investigation of substituent effects on base strength, the hydrogen-bonding ability of a set of 2-monosubstituted pyridines was recently evaluated in this laboratory from ab initio molecular orbital calculations.[10] In that study, the structures and stabilization energies of water–2-R-pyridine complexes (mixed dimers), with R including the isoelectronic saturated groups CH_3, NH_2, OH, and F and the unsaturated groups C_2H_3

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[6] E. M. Arnett in ref 1a, pp 79–101.

[7] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 318 (1976).

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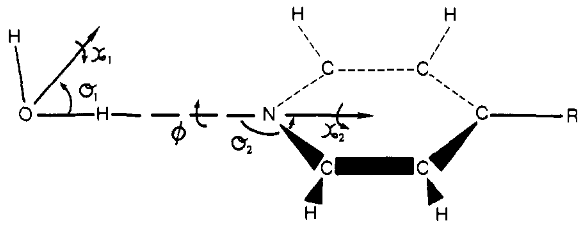

Figure 1. The perpendicular water–4-R-pyridine dimer showing principal axes and intermolecular coordinates. The principal axis of water is the C_2 symmetry axis with origin at the oxygen, while the principal axis of a 4-R-pyridine is the bisector of the C–N–C angle with origin at the nitrogen. The intermolecular angle θ_1 is the angle between the principal axis of water and the O–N line, while χ_1 measures rotation of the water molecule about its principal axis. The angles θ_2 and χ_2 are defined analogously for the 4-R-pyridine. The fifth angle ϕ measures rotation of the 4-R-pyridine about the intermolecular line.

(vinyl), CHO, and CN, were determined. It was shown that the structural and energetic properties of these complexes are influenced by both primary and secondary substituent effects, which could be separately evaluated. Primary substituent effects are those which arise from the influence of the substituent on the electronic environment at the nitrogen, and specifically on the availability of the nitrogen lone pair of electrons for hydrogen-bond formation. Secondary substituent effects arise in hydrogen-bonded complexes from other long-range and dipole interactions. The study of substituent effects on the hydrogen-bonding ability of pyridine bases has now been extended to the set of 4-R-pyridines, with R defined as above. The purpose of the present study is threefold: (1) to determine the equilibrium structures and stabilization energies of the water–4-R-pyridine dimers; (2) to evaluate primary and secondary substituent effects on these structures and stabilities; (3) to compare and contrast the 2- and 4-R-pyridines as proton-acceptor molecules in dimers with water.

Method of Calculation

Single determinant ground state wave functions for the 4-R-pyridines and their hydrogen-bonded complexes have been determined by solving the Roothaan equations,[11] using the STO-3G basis set[12] for the molecular orbital expansions. The equilibrium structures and properties of the 4-R-pyridines have already been reported.[13] With the optimized geometries of the 4-R-pyridines and of water held rigid,[14] the structures of the water–4-R-pyridine dimers have been optimized in the standard intermolecular coordinate system used previously,[15,16] which consists of an intermolecular distance (the O–N distance in these dimers) and five intermolecular angles, defined with reference to the principal axes of the proton-donor and proton-acceptor molecules and the intermolecular line, as shown in Figure 1. Optimization of the dimer structures has been carried out with the restriction that the dimers have the conformation shown in Figure 1, in which the plane of the pyridine ring is perpendicular to the plane of the water molecule. With this constraint, optimization was carried out to ±0.01 Å in the O–N distance and to ±1° in the intermolecular angles. Since the water–4-aminopyridine, water–4-fluoropyridine, and water–4-cyanopyridine dimers have C_s symmetry in this conformation, the perpendicular structure must correspond to an extremum on the intermolecular surface with respect to rotations of the proton-acceptor molecule described by χ_2 and ϕ. For the remaining dimers which are asymmetric, no such relationship holds. However, calculations performed on corresponding planar structures show that the χ_2 and ϕ potential curves are quite flat. The optimized perpendicular structures appear to be minimum-energy structures with respect to changes of ±10° in these coordinates in all cases. For the water–4-R-pyridine dimers, the intermolecular (hydrogen bond) energy is computed as the difference between the total energy of the dimer and the sum of the energies of the isolated monomers. All calculations have been carried out in double precision on an IBM 370/148 computer.

Table I. Structures and Energies of Water–4-R-Pyridine Dimers[a]

	$\theta_1{}'^{b}$	θ_2	R(O–N)	ΔE^c
R = H[d]	−4	175	2.97	−0.007 43
CH_3	−4	175	2.96	−0.007 75
NH_2	−4	176	2.93	−0.008 78
OH	−4	175	2.96	−0.007 72
F	−4	175	2.97	−0.007 23
C_2H_3	−4	175	2.96	−0.007 62
CHO	−4	175	2.98	−0.006 88
CN	−4	175	3.01	−0.006 08

[a] Angles in degrees, O–N distance in angstroms. For these dimers, $\chi_1 = 0°$, $\chi_2 = 90°$, and $\phi = 180°$, giving a trans arrangement of principal axes. See Figure 1. [b] $\theta_1' = \theta_1 - 50°$. $\theta_1' = 0°$ indicates a linear O–H···N bond. [c] ΔE is the intermolecular energy in au. 1 au = 627.49 kcal/mol. [d] Data from ref 15.

Table II. Intermolecular Energies (kcal/mol) of Water–4-R-Pyridine and Water–2-R-Pyridine Dimers

	water–4-R-pyridine		water–2-R-pyridine[a]	
	planar	perpendicular	perpendicular	equilibrium
R = H	4.5	4.7	4.7	4.7
CH_3	4.7	4.9	4.5	4.5
NH_2	5.4	5.5	5.0	6.4
OH	4.7	4.8	3.8	
F	4.4	4.5	4.1	4.4
C_2H_3	4.7	4.8	4.3	4.3
CHO	4.2	4.3	3.9	3.9
CN	3.7	3.8	3.0	3.7

[a] Data from ref 10.

Results and Discussion

Structures. The optimized structures of the water–4-pyridine dimers are reported in Table I. The data show that in each dimer a nearly linear hydrogen bond forms through the nitrogen lone pair of electrons. Thus, these structures are consistent with the idealized structure of the general hybridization model (GHM),[17] which identifies the directed lone pair and the linear hydrogen bond as primary factors determining the equilibrium structure of an open hydrogen-bonded complex. However, these primary factors do not determine the equilibrium conformation of these dimers, since the proton-acceptor molecule may still rotate about its principal axis, leaving the hydrogen bond intact. The equilibrium conformation of water–4-R-pyridine dimers is determined by other secondary factors, and corresponds to the conformation in which the plane of the pyridine ring is perpendicular to that of the water molecule and tilted slightly away from the external non-hydrogen-bonded hydrogen of water, giving a trans arrangement of the principal axes of the hydrogen-bonded pair. This conformation is similar to the equilibrium conformation found for the water–pyridine dimer.[15] However, it should be noted that in each dimer there is essentially free rotation of the substituted pyridine about its principal axis.

A variation in the structures of open hydrogen-bonded complexes is found in intermolecular distances, which generally shorten with increasing hydrogen bond strength. This correlation is also found for the water–4-R-pyridine dimers. The intermolecular distances range from 2.93 Å in the most stable water–4-aminopyridine dimer to 3.01 Å in the water–4-cyanopyridine dimer, which has the weakest hydrogen bond. Thus, the structural data for the equilibrium water–4-R-pyridine dimers suggest that the nature of the substituent influences the equilibrium structures only slightly through a small variation in intermolecular distances.

Energies. The intermolecular energies of the water–4-R-pyridine dimers are reported in Tables I and II. The variation

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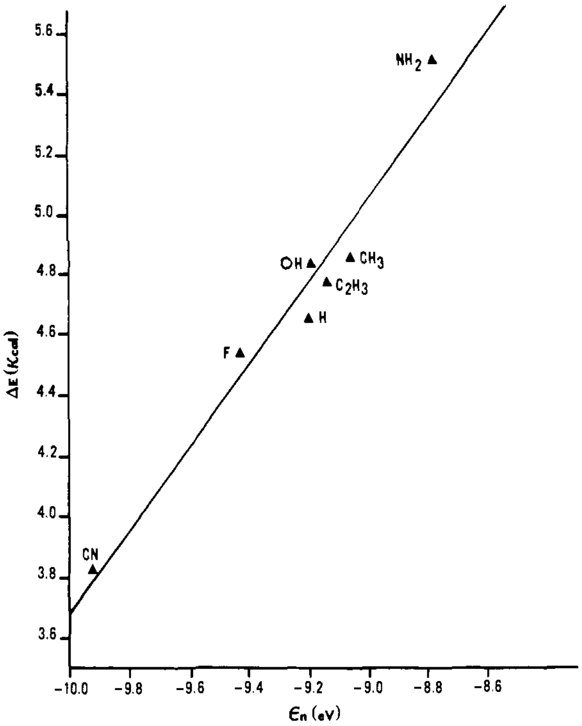

Figure 2. The hydrogen-bond energies of the water–4-R-pyridine dimers vs. the n-orbital energies of the 4-R-pyridines.

of 1.8 kcal/mol in these energies is a direct consequence of the primary electronic effects of the substituents on the pyridine nitrogen. As noted previously,[13] the substituents CH_3, NH_2, OH, F, and C_2H_3 are π-electron-donating and σ-electron-withdrawing groups relative to H, and these σ and π effects have opposing effects on the hydrogen-bonding ability of the pyridine nitrogen. Through π donation, the electron density at the nitrogen increases and the n orbital is destabilized, making the nitrogen lone pair of electrons more available for hydrogen bonding. On the other hand, σ withdrawal decreases the nitrogen electron density and stabilizes the n orbital, thereby tending to decrease the hydrogen-bonding ability of the nitrogen. The data of Table II indicate that the π-donating effect of these substituents from the 4 position generally dominates, since the hydrogen bonds in the water–4-methylpyridine, water–4-aminopyridine, water–4-hydroxypyridine, and water–4-vinylpyridine dimers are stronger than that in the water–pyridine dimer. The strongest hydrogen bond is found in the water–4-aminopyridine dimer, and reflects the strong π-donating ability of the amino group. In contrast, the presence of the σ and π electron-withdrawing groups CHO and CN in the 4 position weakens the hydrogen bond, with the weakest bond occurring in the water–4-cyanopyridine dimer as a result of the strong electron-withdrawing ability of the cyano group. That the σ and π effects of the substituents are the primary factor which influences the hydrogen–bonding ability of these bases by altering the electronic environment at the nitrogen is demonstrated in Figure 2, in which the hydrogen-bond energies of the equilibrium water–4-R-pyridine dimers are plotted against the n-orbital energies of the 4-R-pyridines. A least-squares fit yielded the equation

$$\Delta E = 1.38\epsilon_n + 17.47$$

(where ΔE is the hydrogen-bond energy in kcal/mol, and ϵ_n is the n-orbital energy in eV), with a correlation coefficient of 0.98.[18]

Although the stabilization energies of equilibrium hydrogen-bonded complexes are often influenced by both primary and secondary substituent effects,[10,17,19] the linear correlation evident from Figure 2 demonstrates that secondary substituent effects are not important here. This is also evident from the stabilities of corresponding planar[20] and perpendicular conformations of these dimers, which differ by no more than 0.2 kcal/mol, so that there is essentially free rotation of the substituted pyridine about its principal axis. Although secondary substituent effects may vary with this rotation, the distance between the substituent and the water molecule lessens their importance. The secondary effect which leads to the preferred perpendicular conformation of these dimers is apparently the weak repulsive interaction between the external non-hydrogen-bonded hydrogen of water and the hydrogen atom bonded to C_2 of the ring, which is reduced in the perpendicular relative to a planar conformation.

The hydrogen-bond energies of the water–pyridine, water–4-methylpyridine, and water–4-cyanopyridine dimers obtained in this study may be compared with theoretical and experimental data reported in ref 8. As part of that study, STO-3G calculations were also carried out on these hydrogen-bonded complexes, assuming linear O–H···N hydrogen bonds, and optimizing only H···N distances. The data obtained indicate that methyl substitution in the 4 position of pyridine stabilizes the water–4-methylpyridine dimer by 0.2 kcal/mol relative to the water–pyridine dimer, while substitution of the CN group decreases the stability of the water–4-cyanopyridine dimer by 0.9 kcal/mol relative to the water–pyridine dimer. These data are in agreement with the results of this present study. Experimental heats of solution were obtained and used to estimate the stabilization due to hydrogen bonding of pyridine bases to bulk water. It was estimated that stabilization due to hydrogen bonding to water is 0.4 kcal/mol greater for 4-methylpyridine than for pyridine, but 1.4 kcal/mol less for 4-cyanopyridine than for pyridine. The difference of approximately a factor of 2 between the experimental and theoretical evaluations of substitutent effects on hydrogen bonding was interpreted by the authors as the factor by which bulk water acts as a better hydrogen-bond donor than does a single water molecule.

Electron Populations. Hydrogen-bond formation in the water–4-R-pyridine dimers leads to the expected electron redistribution, as indicated by Mulliken population data.[21] The oxygen and nitrogen atoms which form the O–H···N hydrogen bond gain electron density, while the hydrogen-bonded hydrogen experiences an electron-density loss. Charge transfer occurs from the 4-R-pyridine to the water molecule, and varies from 0.025 e in the water–4-cyanopyridine dimer to 0.036 e in the water–4-aminopyridine dimer. Since the substituent experiences less than a 0.01 e decrease in electron density upon dimer formation, charge transfer from the proton-acceptor molecule occurs primarily at the expense of the pyridine ring.

2- vs. 4-R-Pyridines. Primary substituent effects on the hydrogen-bonding ability of 2-R-pyridines were evaluated previously,[10] and a correlation was established between the n-orbital energies of the 2-R-pyridines and the hydrogen-bond energies of perpendicular water–2-R-pyridine dimers. That result and the analogous linear relationship shown in Figure 2 for the 4-R-pyridines demonstrate that the correlation between n-orbital energies and hydrogen-bond energies for each set of substituted pyridines does not depend on the substituent when the n orbital is essentially localized at the pyridine nitrogen. The nature of primary substituent effects further suggests that this correlation should also be essentially independent of the position of the substituent. That such is the case is demonstrated in Figure 3,

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[18] The data for the water–4-pyridinecarboxaldehyde dimer have been omitted, since the n orbital in 4-pyridinecarboxaldehyde is highly delocalized over the pyridine nitrogen and the carbonyl oxygen, and not, therefore, a suitable measure of the electronic environment at the nitrogen.

[19] J. E. Del Bene, *J. Chem. Phys.*, **57**, 1899 (1972); **62**, 1314 (1975).

[20] The planar structures of the water–4-R-pyridine dimers are described by the optimized intermolecular coordinates determined for the corresponding perpendicular dimer, but with $\chi_2 = 0°$ when the proton-acceptor molecule has C_{2v} symmetry. When it has only C_s symmetry, two planar structures with $\chi_2 = 0$ and 180° are possible. However, these two structures are energetically equivalent to 0.05 kcal/mol. Although the planar structures have not been fully optimized, the energetic equivalence of these structures and the observation that the fully optimized planar water–pyridine dimer does not differ significantly energetically or structurally from the planar dimer described by the intermolecular coordinates of the equilibrium perpendicular structure but with $\chi_2 = 0°$ suggest that the energies of the planar water–4-R-pyridine dimers should not change significantly upon optimization.

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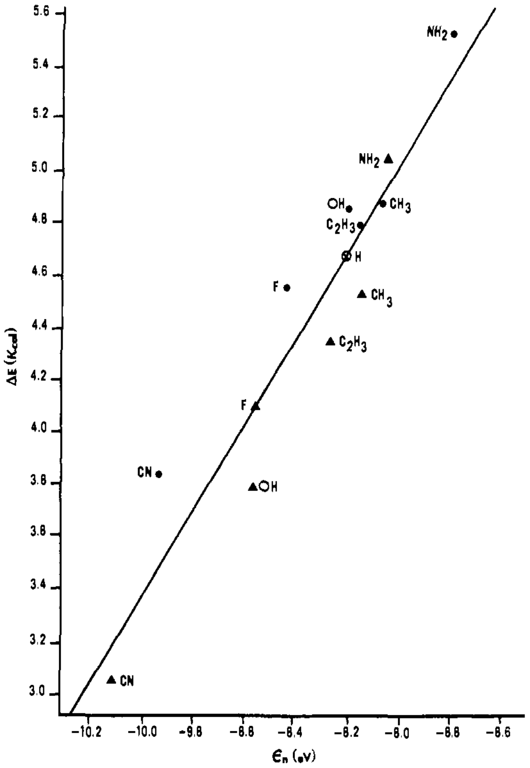

Figure 3. The hydrogen-bond energies of perpendicular water–2-R-pyridine and water–4-R-pyridine dimers vs. the n-orbital energies of the 2- and 4-R-pyridines: ▲, 2-R-pyridine; ●, 4-R-pyridine.

in which the hydrogen-bond energies of the perpendicular water–2-R-pyridine and water–4-R-pyridine dimers are plotted against the n-orbital energies of the pyridine bases. The least-squares equation is

$$\Delta E = 1.66\epsilon_n + 19.93$$

with a correlation coefficient of 0.95. Although this correlation is not as good as that found for the 2- and 4-R-pyridines separately, the linear relationship is clearly evident.

A comparison of the data in Table II for corresponding perpendicular water–2-R-pyridine and water–4-R-pyridine dimers shows that the hydrogen bond in the water–4-R-pyridine dimer is stronger. This parallels the relationship between the n-orbital energies of corresponding 2- and 4-R-pyridines, since the n orbital in the 4 isomer is destabilized relative to the 2 except for 2- and 4-pyridinecarboxaldehyde, in which case n-orbital interaction is also a factor determining the n-orbital energies. These relationships may be attributed to the stronger σ withdrawing effect on the nitrogen electronic environment by substituents in the 2 position relative to the 4, and are consistent with a σ (through-bond) effect which decreases more rapidly with increasing distance than a π (through-space) substituent effect.

Although secondary substituent effects are not significant in the water–4-R-pyridine dimers, they may be quite important in the water–2-R-pyridine dimers, depending on the substituent.[10] Secondary substituent effects are relatively small in the water–2-R-pyridine dimers when R is a nonpolar group, with the result that the water–2-methylpyridine and water–2-vinylpyridine dimers also have perpendicular equilibrium structures. However, the remaining water–2-R-pyridine dimers which have the substituted pyridines as proton-acceptor molecules have planar equilibrium structures stabilized by secondary long-range interactions between the substituent and the water molecule, or by a favorable alignment of the dipole-moment vectors of the hydrogen-bonded pair. Secondary substituent effects stabilize the water–2-fluoropyridine and water–2-cyanopyridine dimers to the extent that they are comparable to the water–4-fluoropyridine and water–4-cyanopyridine dimers, respectively. Secondary effects are even more pronounced in the water–2-aminopyridine dimer, where they lead to a cyclic structure which is 0.9 kcal/mol more stable than the water–4-aminopyridine dimer. These comparisons illustrate that secondary substituent effects ("proximity" effects) in water–2-R-pyridine dimers may have a greater influence on dimer stability than the more direct primary electronic effects of substituents. They vividly illustrate the basis for the lack of correlation found experimentally between substituent effects and rates and equilibria for various chemical reactions involving 2-substituted aromatic rings.

Hydrogen-bond enthalpies have been determined experimentally from IR studies in CCl_4 for some complexes containing methanol as the proton donor and substituted pyridines as proton acceptors.[22] The experimental data indicate that the presence of a methyl group in either the 2 or the 4 position of pyridine strengthens the hydrogen bond, with the strongest bond occurring in the methanol–4-methylpyridine complex. However, the hydrogen-bond enthalpies for the methanol–pyridine, methanol–2-methylpyridine, and methanol–4-methylpyridine complexes vary by only 0.4 kcal/mol. By comparison, the ab initio results indicate that methyl substitution in the 2 position slightly weakens the hydrogen bond in the water–2-methylpyridine dimer relative to the water–pyridine dimer, while substitution in the 4 position leads to a stronger hydrogen bond in the water–4-methylpyridine dimer. Again, only a small 0.4 kcal/mol variation in the hydrogen-bond energies of these complexes is predicted. In the same experimental study, the hydrogen-bond enthalpy for the methanol–2-fluoropyridine complex was found to be 1.6 kcal/mol less than for the methanol–pyridine complex. This result is probably best compared to the decrease of 0.6 kcal/mol in the hydrogen-bond energy calculated for the perpendicular water–2-fluoropyridine dimer relative to the water–pyridine dimer. The underestimation of the experimental value is due in part to the underestimation of the electronegativity of F by the minimal STO-3G basis set.

It has also been observed from both theoretical[23] and experimental[24,25] investigations that n-electron ionization potentials correlate with gas-phase proton affinities when the n orbital is essentially localized at the site of protonation. A correlation has now been established between the n-orbital energies of 2- and 4-R-pyridines and the hydrogen-bond energies of perpendicular water–2-R-pyridine and water–4-R-pyridine dimers. Experimental gas-phase data show that 4-methyl-, 4-fluoro-, and 4-cyanopyridine have higher proton affinities than the corresponding 2 isomers.[26] The order of increasing proton affinity of these substituted pyridines with respect to the substituent and its position is 2-CN < 4-CN < 2-F < 4-F < H < 2-CH_3 < 4-CH_3. This is also the computed order of decreasing n ionization potential, and, except for the reversal of H and 2-CH_3, the computed order of increasing stability of the corresponding perpendicular water–2-R-pyridine and water–4-R-pyridine complexes.

Conclusions

Ab initio SCF calculations have been performed in this study of the structures and stabilities of water–4-R-pyridine dimers, with the substituents including CH_3, NH_2, OH, F, C_2H_3, CHO, and CN. The results of these calculations support the following conclusions.

1. The water–4-R-pyridine dimers are stabilized by nearly linear hydrogen bonds which form through the nitrogen lone pair of electrons. The equilibrium structures of these dimers are similar to the equilibrium perpendicular structure of the water–pyridine dimer, and independent of the nature of the substituent except for a small variation in intermolecular distances. Although the perpendicular conformation is most favorable, rotation of the substituted pyridine about the bisector of the C–N–C angle is essentially free in each dimer.

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2. Except for substitution of F, substitution of a π-electron-donating and σ-electron-withdrawing group for H in the 4 position stabilizes the hydrogen bonds in the water–4-R-pyridine dimers relative to the water–pyridine dimer. In contrast, substitution of the σ and π electron-withdrawing groups CHO and CN weakens the hydrogen bonds in the water–4-pyridinecarboxaldehyde and water–4–cyanopyridine dimers.

3. The variation in the hydrogen-bond energies in the series of water–4-R-pyridine dimers is a direct consequence of the primary electronic effects of the substituents. Secondary substituent effects, which include long–range interactions between the substituent and the water molecule and the relative alignment of the dipole-moment vectors of the hydrogen-bonded pair, are not significant factors determining the equilibrium structures or stabilization energies of these dimers.

4. Primary substituent effects influence the electronic environment at the nitrogen, and are evident from the variation in the n-orbital energies of the pyridine bases. A linear correlation exists between the n-orbital energies of both 2- and 4-R-pyridines and the hydrogen-bond energies of the perpendicular water–2-R-pyridine and water–4-R-pyridine dimers, provided that the n orbital is essentially localized at the nitrogen.

5. The hydrogen bond in the equilibrium perpendicular conformation of a water–4-R-pyridine dimer is stronger than that in the corresponding perpendicular water–2-R-pyridine dimer, due primarily to a stronger destabilizing σ withdrawing effect by the substituent in the 2 position. However, since secondary substituent effects may be important in stabilizing planar water–2-R-pyridine dimers, the 2-R-pyridine may form the more stable complex in particular cases.

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Pauling "3-Electron Bonds", "Increased-Valence", and 6-Electron 4-Center Bonding

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Contribution from the Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia. *Received January 18, 1980*

Abstract: The molecular orbital description of the Pauling "3-electron bond" $\mathbf{A}\cdots\mathbf{B}$ (or $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ according to the Linnett notation) involves two bonding electrons and one antibonding electron. When the antibonding orbitals of $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ and $\dot{\mathbf{C}}\cdot\dot{\mathbf{D}}$ overlap and their electrons are spin-paired, the valence structure


(I)

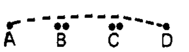
for 6-electron 4-center bonding is generated, which has the following properties: (a) It summarizes resonance between the standard valence-bond structure


(II)

and the "long-bond" (or spin-paired diradical) structures.


(III)


(IV)


(V)

Therefore I is more stable than II, and has a weaker B-C bond. (b) It can involve a total of four electrons in fractional bonding between all pairs of atoms. Therefore relative to the component Lewis–Langmuir structures II–V (each of which has two bonding electrons), I is designated as an "increased-valence" structure. (c) The valencies of atoms B and C can exceed the valencies of unity for these atoms in II. (d) If A and D and B and C are pairs of equivalent atoms, the wave function for I is the covalent component for the lowest energy molecular orbital configuration with three 4-center molecular orbitals doubly occupied. (e) It can be generated from II by delocalizing nonbonding A and D electrons into bonding AB and CD orbitals, i.e.


→ (I)

For the following systems with one or more 6-electron 4-center bonding units, aspects of their electronic structures are illustrated by using "increased-valence" structures: N_2O_4, $C_2O_4^{2-}$, $S_2O_4^{2-}$, N_2O_2, Cl_2O_2, Br_4^{2-}, Ru(II)–N_2–Ru(II), $(RNO)_2$, $(SN)_2$, $Cu_2(CH_3CO_2)_4$,$2H_2O$, Fe(III)–O_2^{2-}–Fe(III) (or $Fe^{II}O_2Fe^{II}$), N_2O_3, and the reaction $Cl + O_3 \rightarrow ClO + O_2$.

Introduction

The molecular orbital description of the Pauling "3-electron bond"[1] $\mathbf{A}\cdots\mathbf{B}$ (or $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ according to the Linnett notation[2]) involves two bonding electrons and one antibonding electron. When overlap integrals are omitted from normalization constants,[3] the maximum net AB bond order is $^1/_2$; the bonding effect of one of the two bonding electrons is cancelled by that of the antibonding electron. With respect to orbital occupations, it can be deduced quite generally[4] that two bonding electrons and one antibonding electron

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(1) (a) L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367, 3225 (1931); (b) "The Nature of the Chemical Bond", 3rd Ed., Cornell University Press, Ithaca, N.Y., Chapter 10.

(2) (a) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961); (b) "The Electronic Structures of Molecules", Methuen, London, 1964, p 57; (c) *Sci. Prog.*, **60**, 1 (1972). Linnett has pointed out that the designation "3-electron bond" is a misnomer because there is effectively only one bonding electron. However, in line with common practice, we shall continue to use this designation, with the adjective "Pauling" to qualify it. But we shall use the Linnett representation $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ rather than $\mathbf{A}\cdots\mathbf{B}$ as the valence structure, thereby emphasizing the point that the Pauling "3-electron bond" involves one bonding electron and two nonbonding electrons. We remind the reader that $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}} \equiv \ddot{\mathbf{A}}\ \dot{\mathbf{B}} \leftrightarrow \dot{\mathbf{A}}\ \ddot{\mathbf{B}}$.

(3) Throughout this paper, we shall for simplicity omit the overlap integrals from the normalizing constants and the orthogonality relationships for molecular orbitals. If overlap is included, the antibonding orbital is more destabilized than is the bonding orbital stabilized. See N. C. Baird, *J. Chem. Educ.*, **54**, 291 (1977); R. D. Harcourt, *Aust. J. Chem.*, **31**, 199 (1978), for discussions of the effect of inclusion of overlap on the energy of a Pauling "3-electron bond".

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