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Molecular Orbital Theory of the Hydrogen Bond. 20. Pyrrole and Imidazole as Proton Donors and Proton Acceptors

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Abstract: Ab initio SCF calculations with a minimal STO-3G basis set have been performed to determine the structures and stabilization energies of hydrogen bonded pyrrole-water and imidazole-water complexes in which pyrrole and imidazole act either as proton donors or as proton acceptors. While imidazole is a stronger proton donor to water than pyrrole, both molecules form stronger N-H...O hydrogen bonds with water than are found in an amide-water complexes. The structures of the pyrrole-water and imidazole-water dimers are similar, as are the nearby regions of the intermolecular potential surfaces. As proton acceptor molecules, pyrrole and imidazole are quite different. While imidazole forms a strong hydrogen bond with water through the nitrogen σ lone pair of electrons in the molecular symmetry plane, pyrrole forms a relatively weak and flexible π complex with water, with hydrogen bond formation occurring preferentially at the C₃-C₄ bond. The O-H...N hydrogen bond in the imidazole-water dimer is stronger than the O-H...N hydrogen bonds found in azine-water complexes, although the imidazole-water intermolecular potential surface in this region resembles the pyridimine-water potential surface. The π hydrogen bond in the pyrrole-water dimer is stronger than that in the ethylene-water dimer.

Introduction

In previous papers of this series,¹ the heterocyclic aromatic azines pyridine, pyridazine, pyrimidine, and pyrazine were investigated as proton acceptor molecules in hydrogen bonded complexes. Pyrrole and imidazole are two other small heterocyclic aromatic compounds which may also form hydrogen bonds, these by acting either as proton donor or as proton acceptor molecules. It is of interest to investigate the hydrogen bonding properties of these molecules to compare and contrast them with each other, with the azines and ethylene as proton acceptors, and with formamide and methyl-substituted formamides as proton donors. Since both pyrrole and imidazole rings are present in important biological systems, their characterization in dimers with water is a necessary first step toward characterizing and understanding their interactions through hydrogen bonding in these more complex systems.

In the present study, ab initio SCF calculations have been performed to determine the structures and stabilization energies of hydrogen bonded pyrrole-water and imidazole-water complexes, and to investigate the nature of the intermolecular potential surfaces surrounding these structures. It is the purpose of this paper to present the results of this study, and to compare pyrrole and imidazole with each other, with the amides as proton donors, and with the azines and ethylene as proton acceptors.

Method of Calculation

The closed-shell ground state wave functions for pyrrole and imidazole and their hydrogen bonded complexes with water have been described by single Slater determinants Ψ

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

constructed from doubly occupied molecular orbitals (MO's).

The MO's ψ_i are expressed parametrically as linear combinations of atomic basis functions ϕ_μ (the LCAO approximation)

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

with the expansion coefficients $c_{\mu i}$ determined by solving the Roothaan equations.² The set of atomic basis functions used in this study is the minimal STO-3G basis set with standard scale factors.³ This basis set has been used previously for studies of hydrogen bonded complexes, thus permitting direct comparisons of computed results.

Because the use of nonoptimized monomer geometries can lead to spurious dimer stabilization,^{4,5} the first step in this investigation was to optimize the pyrrole and imidazole geometries. For pyrrole, C_{2v} symmetry was assumed, and bond lengths and bond angles were optimized cyclicly and independently to ± 0.01 Å and $\pm 1^\circ$, respectively. For imidazole, C_s symmetry was assumed, and bond distances and bond angles were again optimized as in pyrrole. The optimized STO-3G structure of water has been reported previously.⁶

With the constraint that the optimized monomer geometries remain rigid in the hydrogen bonded complexes,⁴ it is possible to describe the relative orientation of the pair of hydrogen bonded molecules in an intermolecular coordinate system in terms of an intermolecular distance R , and five intermolecular angles, defined with reference to an intermolecular line and the principal axes of the proton donor and proton acceptor molecules. For pyrrole, the principal axis has been chosen as the C_2 symmetry axis, coincident with the N-H bond, with origin at the nitrogen atom. For imidazole as a proton donor molecule, the principal axis has been chosen in a similar manner to be coincident with the N₁-H bond, with origin at

Table I. Pyrrole and Imidazole Geometries

		bond distances, Å		bond angles, °		
		calcd	exptl	calcd	exptl	
pyrrole ^a	N ₁ -C ₂	1.38	1.37	C ₂ -N ₁ -C ₅	109	110
	C ₂ -C ₃	1.35	1.38	N ₁ -C ₂ -C ₃	108	108
	N ₁ -H	1.02	1.00	C ₂ -C ₃ -H	126	126
	C-H	1.08 ^b	1.08	C ₃ -C ₂ -H	131	131
	C ₃ -C ₄	1.44 ^c	1.42			
imidazole ^d	N ₁ -C ₂	1.38	1.35	C ₂ -N ₁ -C ₅	107	107
	C ₂ -N ₃	1.32	1.33	N ₁ -C ₂ -N ₃	111	111
	N ₁ -C ₅	1.39	1.37	N ₁ -C ₅ -C ₄	106	106
	C ₄ -C ₅	1.35	1.36	C ₂ -N ₁ -H	127	129
	N ₁ -H	1.02	1.05	N ₁ -C ₂ -H	122	110
	C-H	1.08 ^b	0.96-1.09 ^e	N ₁ -C ₅ -H	122	117
	N ₃ -C ₄	1.40 ^c	1.38	C ₅ -C ₄ -H	128	133

^a Experimental gas phase microwave data taken from ref 7. ^b All computed C-H bond distances assumed equal. ^c X₃-C₄ distances not directly optimized. ^d Experimental X-ray data for solid imidazole taken from ref 8. ^e Experimental C-H distances from ref 8 vary from 0.96 to 1.09 Å.

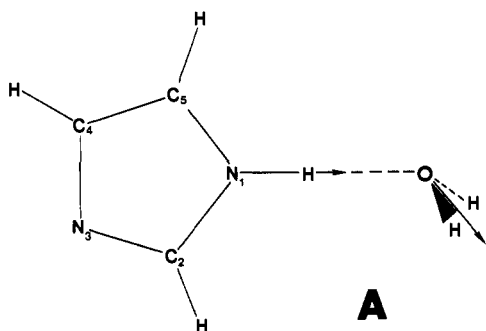


Figure 1. The imidazole-water dimer A showing principal axes.

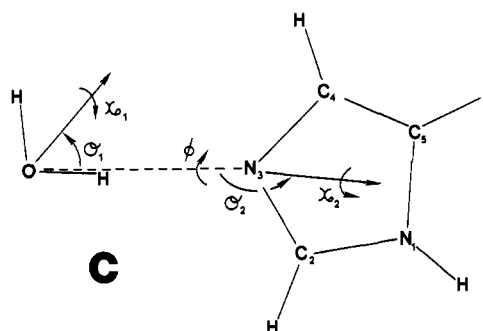


Figure 2. The imidazole-water dimer C showing principal axes and intermolecular coordinates.

the nitrogen, as shown in Figure 1. However, when imidazole is the proton acceptor molecule, a more convenient choice of principal axis is the bisector of the C₂-N₃-C₄ angle, with origin at the nitrogen atom N₃, as shown in Figure 2. For water, the principal axis is the C₂ symmetry axis with origin at the oxygen.

In the intermolecular coordinate system, the line connecting the origins of the principal axes of the proton donor and proton acceptor molecules is the intermolecular line, and the distance between origins is the intermolecular distance parameter *R*. The intermolecular angle θ_1 is the angle between the principal axis of the proton donor molecule and the intermolecular line, while the angle χ_1 is the angle which measures rotation of the proton donor molecule about its principal axis. The angles θ_2 and χ_2 are defined similarly for the proton acceptor molecule. The fifth angle ϕ measures rotation of the principal axis of the proton acceptor molecule about the intermolecular line. These angles are shown in Figure 2. In the hydrogen bonded complexes, the intermolecular distance has been optimized to ± 0.01 Å, and the intermolecular angles to $\pm 1^\circ$, where possible. The intermolecular (hydrogen bond) energy is computed as the difference between the total dimer energy and the energy of the isolated monomers. All calculations have been performed in double precision on IBM 370/145 or 370/148 computers.

Results and Discussion

Monomers. The computed equilibrium structures of pyrrole and imidazole are reported in Table I along with the available experimental data. As evident from this table, the computed structure of pyrrole is in excellent agreement with the experimental gas-phase structure obtained from microwave spec-

troscopy.⁷ The only significant difference between computed and experimental geometrical parameters is in the relationship of the N₁-C₂ and C₂-C₃ bond distances. While the experimental C₂-C₃ distance is 0.01 Å longer than the N₁-C₂ distance, the computed C₂-C₃ distance is 0.03 Å shorter than the N₁-C₂ distance. The computed dipole moment of 1.82 D is slightly greater than the experimental value of 1.74 D.⁷

The agreement between the computed structure of imidazole and the experimentally determined structure in the solid state⁸ is not as good as that between the computed and the experimental gas-phase structure of pyrrole. While theoretical and experimental bond distances and angles within the imidazole ring are in fairly good agreement, there are large discrepancies between theoretical and experimental bond distances and angles which describe the positions of hydrogen atoms. These discrepancies are most probably due to the uncertainty in the hydrogen atom positions as determined by X-ray diffraction, and also to the intermolecular forces in the solid, which may have significant structural effects, especially on the peripheral hydrogen atoms. The computed dipole moment of imidazole is 3.54 D, which is about double that of pyrrole, and smaller than the experimental value of 4.02 D.⁹ The computed dipole moment vector is within 2° of being coincident with the N₁-N₃ line, with the negative end nearer the nitrogen atom N₃.

Pyrrole and Imidazole as Proton Donors. The structures of the pyrrole-water and imidazole-water complexes in which pyrrole and imidazole are the proton donor molecules are reported in Table II, and the imidazole-water dimer is shown in Figure 1. The computed equilibrium dimers of C_s symmetry have structures which are consistent with the general hybridization model (GHM)¹⁰ which describes an idealized hydrogen bond as arising when a directed lone pair of electrons on the

Table II. Structures and Stabilization Energies of Pyrrole–Water and Imidazole–Water Complexes with Pyrrole and Imidazole as Proton Donors

	θ_1 , deg	χ_1 , deg	θ_2 , deg	χ_2 , deg	ϕ , deg	R , Å	ΔE , au ^a
pyrrole–water							
dimer A	1	0	130	90	180	2.69	−0.01305
dimer B ^b	2	90	128	90	180	2.69	−0.01288
imidazole–water							
dimer A	1	180	132	90	180	2.66	−0.01523
dimer B	1	0	132	90	180	2.66	−0.01515

^a ΔE is the intermolecular (hydrogen bond) energy. 1 au = 627.49 kcal/mol. ^b Not an equilibrium structure.

proton acceptor atom Y takes part in the formation of a linear X–H...Y bond. Thus, the values of the coordinate θ_1 which are near 0° indicate that the N–H...O hydrogen bonds in these dimers are linear. The values of $\chi_2 = 90^\circ$ place the oxygen lone pairs in the dimer symmetry plane, and values of $\theta_2 = 130$ and 132° in the pyrrole–water and imidazole–water dimers, respectively, direct one of these lone pairs toward the proton donor molecule along the intermolecular line. These values of the coordinate θ_2 are somewhat larger than the idealized GHM value (125°) and that computed (123°)¹¹ and found experimentally (122°)¹² for the water dimer. A similar orientation of the water molecule was found in the amide–water dimers which also contain N–H...O hydrogen bonds.¹⁰ It appears that as the proton donor molecular dipole moment or its component along the N–H bond increases, the dipole–dipole interaction, a secondary factor in dimer stabilization, assumes increased importance. As a result, the proton acceptor water molecule tends to rotate slightly away from the proton donor in the direction of increasing θ_2 .¹³

In the pyrrole–water dimer, the N–H bond of pyrrole is, for all practical purposes, coincident with the intermolecular line. As a result, rotation of pyrrole about the N–H bond (the χ_1 , rotation about the principal axis), and rotation of the water molecule about the intermolecular line (the ϕ rotation) leave the hydrogen bond intact. In addition, since the dipole moment vector of pyrrole is also coincident with the N–H bond, these rotations do not produce changes in the relative orientation of the dipole moment vectors of pyrrole and water, nor do they lead to significant changes in long-range interactions. Thus, these rotations should be and are essentially free. Along the χ_1 coordinate from the equilibrium dimer A, an equivalent dimer is found at $\chi_1 = 180^\circ$, while along the ϕ coordinate, another occurs at $\phi = 0^\circ$. The rotational barriers along these coordinates, estimated from the energy of dimer B (see Table II) which was optimized subject to the constraint that the molecular planes be perpendicular, are approximately 0.1 kcal/mol.

In those regions of the intermolecular potential surfaces where pyrrole and imidazole are proton donors, the imidazole–water and pyrrole–water surfaces are similar. However, there are differences between these two surfaces, which are related to the different orientations of the dipole moment vectors of pyrrole and imidazole. In imidazole, the dipole vector is not coincident with the N–H bond as in pyrrole, but makes an angle of about 18° with this bond. Consequently, in the imidazole–water dimer, rotation of imidazole about the N–H bond (the χ_1 rotation about the principal axis) and rotation of the water molecule about the intermolecular line (the ϕ rotation) lead to small changes in the relative orientation of the dipole moment vectors of imidazole and water, with the result that nonequivalent equilibrium structures exist along both the χ_1 and ϕ coordinates. Dimers labeled A and B in Table II are the two equilibrium structures, in which the nitrogen atom N₃ is cis and trans, respectively, to the water hydrogens with respect to the intermolecular line. Structure A, illustrated in Figure 1, has the more favorable dipole alignment, and is

slightly more stable than B, but by less than 0.1 kcal/mol. The rotational barrier along the χ_1 coordinate separating dimers A and B, estimated from the energy of a dimer having the intermolecular coordinates of A but with $\chi_1 = 90^\circ$, is less than 0.2 kcal/mol.

The hydrogen bonds in the pyrrole–water and imidazole–water complexes are very strong, as indicated by the hydrogen bond energies of 8.2 and 9.6 kcal/mol, respectively. These hydrogen bond energies are even more striking when compared to the computed N–H...O hydrogen bond energies of the ammonia–water dimer (4.1 kcal/mol)¹⁴ and the amide–water dimers (5.8–6.4 kcal/mol).¹⁰ The strong proton-donating ability of pyrrole and imidazole is a consequence primarily of the acidity of the N–H protons in these molecules, which have positive charges of 0.215 and 0.225 e , respectively, as determined by Mulliken population analyses.¹⁵ These charges are significantly larger than the positive charges on the N–H protons in ammonia (0.147 e), and in formamide and methyl-substituted formamides (0.186–0.196 e). An increased positive charge on the proton leads to an increased electrostatic interaction, which stabilizes hydrogen bonded complexes. The large positive charges on the hydrogens and the strong proton-donating ability of pyrrole and imidazole suggest that the N–H groups in these molecules have considerable ammonium-like character.¹⁶ It is also apparent that while both of these molecules are strong proton donors in hydrogen bonded complexes with water, imidazole is a stronger donor than pyrrole. Its greater proton-donating ability may also be attributed to its more acidic proton, and to its larger dipole moment. These characteristics of imidazole are a direct result of introducing a second nitrogen atom into the pyrrole ring.

Hydrogen bond formation leads to a redistribution of electron density in hydrogen bonded complexes. In the pyrrole–water and imidazole–water dimers, this includes charge transfer from the proton acceptor water molecules to the proton donors, as evident from the Mulliken population data reported in Table III. The amount of charge transfer is greater in the imidazole–water dimer than in the pyrrole–water dimer, as anticipated from the greater stability of the former. In both complexes, hydrogen bond formation has its greatest effect on the electron densities of the nitrogen and hydrogen atoms which form the N–H...O bonds, with the former gaining and the latter losing electron density relative to the monomers. As a result of hydrogen bonding, all atoms in the aromatic rings experience an increase of electron density, with the greatest increase occurring at the hydrogen bonded nitrogen atoms. However, while the total electron densities of these nitrogens increase, their π densities decrease, as hydrogen bonding leads to a polarization of π electron density away from N₁. In the imidazole–water dimer, hydrogen bonding also produces an increase in the total and the π electron densities of N₃. This suggests that the ability of imidazole to form a hydrogen bond as a proton acceptor molecule is enhanced when it is also acting as a proton donor through the N–H proton.

Pyrrole and Imidazole as Proton Acceptors. The structures and hydrogen bond energies of the pyrrole–water and imid-

Table III. Mulliken Gross Populations

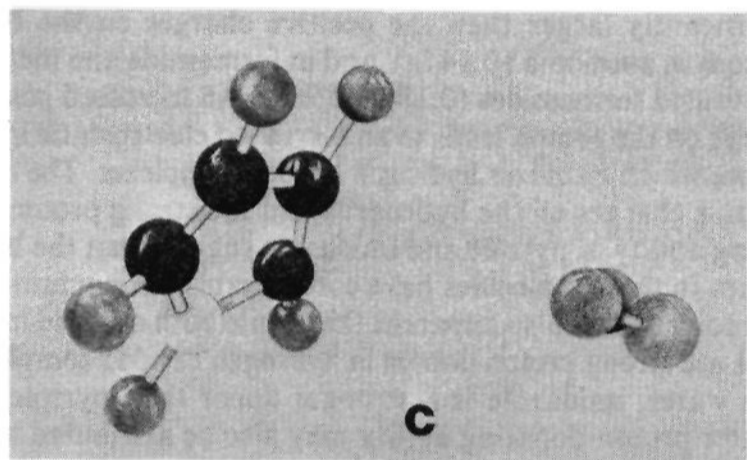
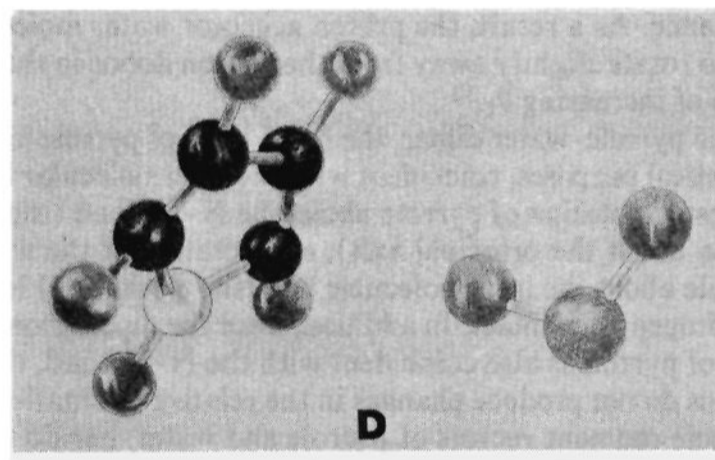
	N ₁		C ₂		X ₃ ^a		C ₄		C ₅		H ^b	O	charge transfer ^c
	total	π	total	π	total	π	total	π	total	π			
pyrrole-water													
monomer	7.307	1.643	5.978	1.088	6.101	1.090	6.101	1.090	5.978	1.088	0.785	8.330	
dimer A	7.339	1.616	5.984	1.087	6.109	1.103	6.107	1.100	5.989	1.095	0.746	8.329	0.059
dimer C	7.306		5.979		6.108		6.108		5.979		0.780	8.340	0.006
imidazole-water													
monomer	7.311	1.633	5.876	1.060	7.269	1.131	6.022	1.093	5.986	1.084	0.775	8.330	
dimer A	7.344	1.604	5.889	1.070	7.281	1.138	6.030	1.105	5.993	1.083	0.736	8.330	0.066
dimer C	7.308	1.627	5.865	1.042	7.281	1.160	6.018	1.091	5.981	1.079	0.768	8.377	0.035

^a X₃ is C₃ in pyrrole and N₃ in imidazole. ^b The N-H proton. ^c Electron transfer to the proton donor molecule.

Table IV. Structures and Stabilization Energies of Pyrrole-Water and Imidazole-Water Complexes with Pyrrole and Imidazole as Proton Acceptors

	θ ₁ , deg	χ ₁ , deg	θ ₂ , deg	χ ₂ , deg	φ, deg	R, Å	ΔE, ^a au
pyrrole-water							
dimer C	33	90	118	90	180	3.94	-0.00234
dimer D ^b	69 ^c	0	117	90	180	4.07	-0.00211
imidazole-water							
dimer C	48 ^c	0	174	180	180	2.94	-0.00898
dimer D ^b	46 ^c	0	176	0	180	2.94	-0.00853

^a ΔE is the intermolecular (hydrogen bond) energy. 1 au = 627.49 kcal/mol. ^b Not an equilibrium structure. ^c (θ₁ - 50°) is the angle between the O-H bond and the O-N line.

**Figure 3.** The pyrrole-water π dimer C.**Figure 4.** The pyrrole-water π dimer D.

azole-water dimers which have pyrrole and imidazole as proton acceptor molecules are reported in Table IV. The stabilization energy of 5.6 kcal/mol for the imidazole-water dimer C arises from the formation of a strong hydrogen bond at N₃ through the nitrogen lone pair of electrons in the σ electron system of imidazole. The significantly smaller stabilization energy of 1.5 kcal/mol for the pyrrole-water dimer C arises from the formation of a weak π hydrogen bond through the π electron system of pyrrole. Thus, pyrrole and imidazole are distinctly different as proton acceptor molecules, and the pyrrole-water and imidazole-water intermolecular potential surfaces are very different in these regions.

The search of the pyrrole-water intermolecular surface led to the identification of two hydrogen bonded structures of C_s symmetry, labeled C and D in Table IV. The more stable dimer C, shown in Figure 3, is one in which the water molecule is a double proton donor to pyrrole, with the water hydrogens directed toward the C₃-C₄ bond of pyrrole. In this dimer, the plane of the water molecule is nearly perpendicular to the plane of the pyrrole ring, as these planes intersect at an angle of 85°, with the plane of the water molecule inclined slightly toward the nitrogen. While the intermolecular O-N₁ distance is 3.94 Å, the distance between the oxygen atom and the midpoint of the C₃-C₄ bond is about 3.5 Å. This distance is 0.1 Å shorter

than that found in the ethylene-water π dimer in which water is also a double proton donor.¹⁷

The second pyrrole-water π dimer, labeled D in Table IV, is one in which only one of the hydrogen atoms of water is hydrogen bonded to pyrrole through the π system, as shown in Figure 4. In this dimer, the hydrogen bonded proton is directed toward the center of the pyrrole ring. The angle between the O-H bond and the plane of the ring is 98°, with the O-H bond tilted slightly away from the nitrogen. The external O-H bond of water is nearly parallel to the plane of the pyrrole molecule. While dimer D is a stable structure with respect to changes in each of the intermolecular coordinates, it is not an equilibrium structure on the intermolecular surface, but is located at a saddle point. There exists a direct path along the surface by which dimer D may be converted to dimer C with no energy barrier.

The structure of the equilibrium pyrrole-water dimer C is very similar to the equilibrium structure of a pyrrole-HF π dimer in which pyrrole is also the proton acceptor molecule.¹⁸ In the pyrrole-HF dimer, the HF molecule is oriented so that it is nearly perpendicular to the plane of the pyrrole ring (the angle between the HF line and this plane is 86°, with the HF molecule inclined slightly toward the nitrogen), and the HF proton is directed toward the C₃-C₄ bond. The intermolecular

energy of this dimer is 1.7 kcal/mol. This dimer is 1.0 kcal/mol more stable than a nonequilibrium pyrrole-HF π dimer optimized under the constraint that the HF molecule be perpendicular to the pyrrole ring at the nitrogen atom.

The most interesting feature of the pyrrole-water and the pyrrole-HF dimers is that the π hydrogen bonds in these complexes do not form at the nitrogen atom. From electrostatic considerations, it might have been expected that the nitrogen would be the preferred site of hydrogen bonding, as it has the largest negative charge and the highest π electron density, as shown in Table III. That these π hydrogen bonds do not form preferentially at the nitrogen suggests that the nitrogen π electron density is relatively tightly bound and not available for transfer to the proton donor molecule. This lack of nucleophilic character may be related to the nature of the highest occupied molecular orbital of pyrrole, a π orbital of a_2 symmetry, which has a node through the nitrogen atom. Thus, it appears that electron transfer to the proton donor molecule, which is also a factor in stabilizing hydrogen bonded complexes, may occur more easily through the carbon atoms, with C₃ a better electron donor than C₂, as C₃ has a negative charge of 0.101e while C₂ bears a small positive charge of 0.022e.¹⁹

A second interesting feature of the interaction of pyrrole and water through the pyrrole π electron system is the flatness of the intermolecular potential surface in this region. The equilibrium pyrrole-water dimer C is found in a relatively shallow minimum (1.5 kcal/mol), and the surrounding surface is quite flat except for the rotation which moves the pyrrole ring away from the water molecule (the rotation which decreases θ_2). Dimer D, which is found at a saddle point on the surface, has a hydrogen bond energy of 1.3 kcal/mol. A dimer in which water is a double proton donor to pyrrole at the C₂-C₃ bond has a hydrogen bond energy of 1.1 kcal/mol, while another dimer with hydrogen bonding occurring through the N₁-C₂ bond has a stabilization energy of 0.7 kcal/mol.²⁰ These data indicate that there is considerable flexibility in the orientation of a solvent molecule such as water which interacts with pyrrole through its π electron system. They also indicate that while the delocalized π electrons of pyrrole form weak hydrogen bonds, these are significantly stronger than the π hydrogen bond in the ethylene-water complex, which has an energy of only 0.5 kcal/mol.¹⁷

In the equilibrium imidazole-water dimer, labeled C in Table IV and shown in Figure 2, hydrogen bond formation occurs through the nitrogen lone pair of electrons in the σ electron system of imidazole. The importance of having a compact region of high electron density (a σ lone pair) for hydrogen bond formation is demonstrated by comparing the stability of this dimer (5.6 kcal/mol) with that of the pyrrole-water π dimer (1.5 kcal/mol). The stabilization energy of the imidazole-water dimer also indicates that the hydrogen bond in this dimer is significantly stronger than the O-H...N hydrogen bonds formed through the nitrogen σ lone pairs in the azine-water complexes, which have stabilization energies ranging from 3.7 to 4.7 kcal/mol.¹ The greater stability of the imidazole-water dimer correlates with the greater total and π electron densities at the proton acceptor nitrogen atom N₃. This is a direct result of the presence of the pyrrolic nitrogen N₁ which is a π electron donor to the aromatic system.

The imidazole-water dimer C has planar C_s symmetry, with the N-H bond of imidazole trans to the external O-H bond of water with respect to the intermolecular line, as shown in Figure 2. The structure of this dimer is consistent with that anticipated from the general hybridization model. While the imidazole-water dimer C is an equilibrium structure on the intermolecular surface, barriers to rotation of imidazole about its principal axis (the χ_2 rotation) and of the principal axis of imidazole about the intermolecular line (the ϕ rotation) are

small, since these rotations leave the hydrogen bond essentially intact and do not result in significant changes in dipole alignments or long-range interactions. It is not surprising then, that an imidazole-water dimer optimized under the constraint that the plane of the imidazole molecule be perpendicular to the plane of the water molecule²¹ is energetically equivalent to dimer C. This dimer is readily obtained from dimer C through a 90° rotation of imidazole about its principal axis. A further 90° rotation leads to dimer D, which is a nonequilibrium structure on the surface. This dimer, in which the N-H bond of imidazole is now cis to the external O-H bond of water, has a stabilization energy of 5.3 kcal/mol. Estimated from this dimer, the χ_2 rotational barrier is about 0.3 kcal/mol. The decreased stability of dimer D may be attributed to a less favorable alignment of the dipole moment vectors of water and imidazole in this dimer compared with dimer C. The imidazole-water potential surface in this region appears to be similar to the pyrimidine-water surface in that region where pyrimidine is the proton acceptor molecule.¹

In the imidazole-water dimer C, charge transfer occurs from imidazole to water through the σ electron system. As a result of hydrogen bond formation, the nitrogen and oxygen atoms which form the O-H...N hydrogen bond become more negatively charged, while the hydrogen bonded proton becomes more positively charged. As apparent from Table III, the increase in the electron density at N₃ is a result of π electron polarization toward this atom, which occurs at the expense of the other atoms in the ring. This type of π electron polarization was also found in the azine-water dimers, and is opposite to the polarization which occurs when imidazole is the proton donor molecule in the imidazole-water dimer A. In addition, in the imidazole-water dimer C, hydrogen bond formation through the nitrogen atom N₃ leaves the hydrogen which is bonded to N₁ more positively charged than it is in the monomer. Hence, it would be anticipated that hydrogen bond formation through N₃ would also enhance the proton donating ability of imidazole through the N-H proton.

Conclusions

The following conclusions are supported by the results of this study.

(1) Pyrrole and imidazole are similar as proton donor molecules in hydrogen bonded complexes with water, where linear N-H...O hydrogen bonds are formed through a lone pair of electrons on the oxygen atoms. The nearby regions of the pyrrole-water and imidazole-water intermolecular potential surfaces are also very similar, and are characterized by essentially free rotation of the proton donor molecules about the N-H bonds, and of the proton acceptor molecules about the intermolecular O-N lines.

(2) Both pyrrole and imidazole are very strong proton donors in complexes with water, as the N-H...O hydrogen bond energies in the pyrrole-water and imidazole-water dimers (9.6 and 8.2 kcal/mol, respectively) are significantly greater than the N-H...O hydrogen bond energies in the ammonia-water dimer (4.1 kcal/mol) and in the amide-water dimers (5.8-6.4 kcal/mol). The stronger proton donating ability of imidazole correlates with the greater positive charge on its N-H proton, and with its larger dipole moment.

(3) Pyrrole and imidazole are very different as proton acceptor molecules in dimers with water. While a strong hydrogen bond of 5.6 kcal/mol forms through the nitrogen σ lone pair of electrons in the imidazole-water complex, a weak π hydrogen bond of 1.5 kcal/mol forms through the π electron system of pyrrole in the pyrrole-water complex.

(4) Imidazole forms a stronger O-H...N hydrogen bond with water than do the azine molecules pyridine, pyridazine, pyrimidine, and pyrazine, as the stabilization energies of the azine-water complexes range from 3.7 to 4.7 kcal/mol. The

orientation of the imidazole molecule in the imidazole-water dimer is quite flexible with respect to rotation of imidazole about its principal axis and about the intermolecular O-N line. The imidazole-water intermolecular potential surface resembles the pyrimidine-water surface in the region where pyrimidine is the proton acceptor molecule.

(5) Pyrrole forms stronger hydrogen bonds through its π electron system than ethylene, as indicated by the stabilization energies of 1.5 and 0.5 kcal/mol for the pyrrole-water and ethylene-water dimers, respectively. The most stable pyrrole-water π dimer is one in which water is a double proton donor, with π hydrogen bond formation occurring at the carbon atoms C₃ and C₄ and not at the nitrogen. The surrounding intermolecular surface is relatively flat, indicating that there is considerable flexibility in the orientation of the hydrogen bonded molecules.

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 (18) The intermolecular coordinates for the pyrrole-HF dimer are $\theta_1 = 34^\circ$, $\theta_2 = 120^\circ$, $\chi_2 = 90^\circ$, $\phi = 180^\circ$, and $R = 3.97 \text{ \AA}$.
 (19) The amount of charge transfer in dimer C is very small (0.006e), as expected when hydrogen bonds are weak. However, the standard pattern of electron density changes upon hydrogen bond formation is discernible. Specifically, the electron densities of the oxygen atom in the proton donor molecule and of the carbon atoms C₃ and C₄ increase, while those of the hydrogen bonded protons decrease.
 (20) In these dimers, the water molecule is perpendicular to the pyrrole ring at the C₂-C₃ and N₁-C₂ bonds, respectively. These dimers were optimized with respect to the distance between the oxygen atom and the midpoints of these bonds. The optimized distances are about 3.55 Å.
 (21) This dimer has optimized intermolecular coordinates $\theta_1 = 45^\circ$, $\theta_2 = 176^\circ$, and $R = 2.94 \text{ \AA}$.

Ground States of Molecules. 48. MINDO/3 Study of Some Radical Addition Reactions¹

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Abstract: The potential surfaces for the additions of methyl radicals to ethylene, acetylene, propene, and allene have been studied, using MINDO/3. The calculated activation energies agree well with experiment, as do the predicted points of attack in propene and allene. The transition states have unusual structures, being reactant-like except for the attacking methyl which has a product-like pyramidal geometry. This accounts for apparent contradictions in the experimental evidence.

The addition of alkyl radicals to multiple bonds is a process which has attracted much attention.² These reactions take place rapidly, having rate constants of the order of 10^3 - $10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ at ambient temperatures,^{2,3} activation energies⁴ in the range $6 \pm 2 \text{ kcal/mol}$, and Arrhenius preexponential factors⁴ between 10^6 and 10^9 . While polar and steric effects play a role in determining the rate and direction of addition to a given double or triple bond, the determining factor in most cases seems to be the exothermicity of the reaction. In particular, the direction of addition to a given double or triple bond is usually that which leads to more stable product.

While the stereochemistry of these reactions has been extensively studied,⁵ there is still uncertainty concerning their detailed mechanisms. It was formerly thought that the reagents first combine to form a π complex, or that a structure of this kind might represent the transition state, but arguments based on simple LCAO-MO theory make this unlikely.⁶ The ex-

perimental evidence currently available seems to suggest that the optimum mode of approach of the alkyl group is along a line through one of the terminal atoms of the multiple bond and perpendicular, or almost perpendicular, to the nodal plane of the π MO involved in the reaction.⁷ Toward the end of the reaction, there must of course be a reorganization of the atom undergoing attack from trigonal to tetrahedral geometry (or digonal to trigonal in the case of addition to a triple bond). The question then arises, what point along this path corresponds to the transition state? If the transition state occurs early, the unsaturated molecule will more or less retain its initial geometry and the transition state will be reactant-like, whereas a late transition state will have a structure similar to that of the product.

Studies⁸ of secondary deuterium isotope effects in the additions of methyl radicals to olefins, and to deuterated olefins, in the gas phase suggest that the transition states are reac-