

The Hydrogen Bond between Water and Aromatic Bases of Biological Interest: An Experimental and Theoretical Study of the 1:1 Complex of Pyrimidine with Water

Sonia Melandri,[†] M. Eugenia Sanz,^{†,‡} Walther Caminati,^{*,†} Paolo G. Favero,[†] and Zbigniew Kisiel[§]

Contribution from the Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna, Via Selmi 2, I-40126 Bologna, Italy, Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain, and Institute of Physics, Polish Academy of Sciences, Al.Lotników 32/46, 02-668 Warszawa, Poland

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Abstract: The supersonic molecular beam (absorption millimeter wave and microwave Fourier transform) spectra of the 1:1 complex between pyrimidine and four isotopomers of water (H₂O, HDO, D₂O, and H₂¹⁸O) have been assigned. The derived moments of inertia are consistent with a planar (or nearly planar) structure of the adduct in which one hydrogen of the water molecule is bound to the nitrogen of the aromatic ring, and the "free" water hydrogen is *entgegen* to the ring. Only high level ab initio calculations (6-31G**+MP2-BSE) account for the coplanarity of the water with the ring molecule. The hydrogen bond stretching force constant and the dissociation energy have been derived to be $k_s = 13.8 \text{ Nm}^{-1}$ and $\Delta E = 21.4 \text{ kJ/mol}$, respectively.

Introduction

Intermolecular interactions and, in particular, hydrogen bonds are of fundamental importance in various processes of chemistry and biology.¹ Spectroscopic studies of weakly bound intermolecular complexes at conditions of supersonic expansion have provided a wealth of information on the structures and dynamics of such species,² and define a starting point for detailed understanding of macroscopic phenomena.

An important area in the study of intermolecular interactions is solvation of aromatic molecules. The application of spectroscopy in such studies has recently been the subject of a thorough review.³ It is clear that there are a vast number of systems that can be studied and a variety of experimental techniques that can be used. It is important, therefore, to select systems which can serve as useful prototypes of important and unique properties. The most direct experimental approach to structure and dynamics in such systems is probably through study of spectra with fully resolved rotational structure.

The prototype system for the study of the interaction of water with an aromatic molecule is benzene–water. The rotational spectra of the 1:1 complex of benzene with several isotopomers of water have been obtained in supersonic expansions.^{4,5} These

studies show that the water molecule is located above the benzene plane, with both hydrogen atoms pointing toward the π cloud (O–H $\cdots\pi$ hydrogen bond) and undergoing nearly free internal rotation. Owing to the complexity of its internal dynamics the geometry of benzene–water is only convincingly explained at a high level of ab initio theory in terms of a quantum mechanical probabilistic structure.⁶

Pyrrrole–water represents another example of a hydrated aromatic molecule. The study of its molecular beam Fourier transform microwave (MBFTMW) spectrum revealed that the monomer molecules are connected through an N–H \cdots O hydrogen bond.⁷

The larger, six-membered, nitrogenated aromatic rings are of particular importance since they are known to constitute key building blocks of proteins and nucleotides. This type of aromatic ring possesses two different proton–acceptor sites: the ring π cloud and the lone pairs on the heteroatoms. Evidence for hydrogen bond formation between a nitrogen lone pair and the water hydrogen has been obtained spectroscopically by observation of the electronic spectrum of pyrazine in solution⁸ and in an argon matrix.⁹ Extensive efforts to observe the formation of clusters of pyrazine and pyrimidine with water in a supersonic expansion were unsuccessful.¹⁰ Recently we investigated the pyrazine–water system with the free jet absorption microwave technique.¹¹ The rotational spectrum of the 1:1 complex was assigned and the structure was determined to be planar with an O–H \cdots N hydrogen bond. The observed

[†] Università degli Studi di Bologna.

[‡] Permanent address: Universidad de Valladolid.

[§] Polish Academy of Sciences.

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perturbations in the rotational spectrum were interpreted in terms of large-amplitude motions of the water moiety.

The pyrimidine ring (PRM) provides an even closer approximation than pyrazine to structural features found in a variety of important biological molecules. It is, in particular, the main constituent of nucleotides. The weak interactions of this molecule with rare gas atoms have been characterized by the electronic^{12,13} and rotational spectra¹⁴ of its complex with Argon. From the electronic spectra^{12,13} the mechanism of the dissociation process has been revealed and the van der Waals bond energy has been estimated. The inertial parameters derived from the rotational spectrum¹⁴ contain information on the structure and the vibrational van der Waals modes that was extracted by using an appropriate model which takes into account also vibration-rotation Coriolis interactions. Such detailed analysis is not available for the interactions between PRM and water, although matrix isolation FT-IR studies and ab initio calculations suggest the presence of N \cdots H-O H bonds in the pyridine-water and pyrimidine-water (PRM-W) complexes.¹⁵

In this work we report the observation and analysis of rotational spectra of the 1:1 complex between pyrimidine and water (PRM-W) together with results of ab initio and modeling calculations which give insight into the intermolecular potential energy surface. The aim of this study is to establish experimentally the structure of the isolated complex and to arrive at an understanding of the intermolecular interactions governing the association process that can be regarded as a prototype for the solvation of heterocyclic aromatic rings containing nitrogen.

Experimental Strategies

The simple, yet versatile technique of supersonic expansion¹⁶ has been used to generate molecular clusters, at conditions optimized for 1:1 cluster formation. Two different experimental setups have been used: a millimeter-wave free jet absorption spectrometer (Bologna), and a molecular beam Fourier transform microwave spectrometer (Warsaw), which provided complementary results.

(a) **Free Jet Absorption Millimeter Wave Spectroscopy.** The Stark and pulse modulated free jet absorption millimeter-wave spectrometer used in this study has already been described elsewhere.^{17,18} The adducts were formed by flowing argon, at room temperature and at a pressure of ca. 0.7 bar, over a solution of PRM and water at a molecular ratio of 2/1. The mixture was then expanded to about 5×10^{-3} mbar through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm, reaching an estimated "rotational" temperature of about 10 K. The high speed of the scans (10 GHz/day) and the near-Boltzmannian intensity of lines allow rapid acquisition of spectra and simplify their assignment.

(b) **MB-FTMW Spectroscopy.** The sample was prepared by expanding a gas mixture obtained by combining two streams of Argon carrier gas, each flown over a container with one of the monomers, at a backing pressure of 0.5–0.7 bar. To minimize the consumption of pyrimidine the flow over the water sample was set to be considerably larger, and the water was chilled to 0 °C so that its partial pressure would not exceed 2%. The gas mixture was pulsed at a rate of 2 Hz,

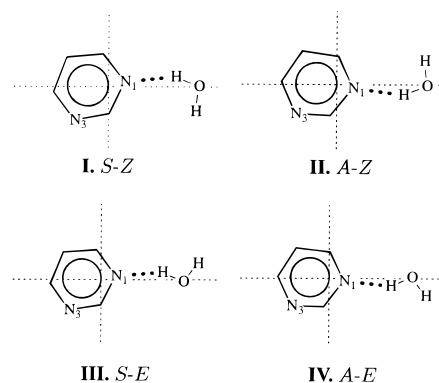


Figure 1. The four possible conformers for the PRM-water adduct predicted on the basis of the structure observed for pyrazine-water. Species AE is the observed one.

through a nozzle with an orifice of 0.35 mm, into the microwave cavity of a spectrometer, giving rise to spectra with an estimated rotational temperature of 1 K. The spectrometer operates over the frequency range 2–18.5 GHz and has been described in detail previously.^{19,20}

Assignment and Characteristics of the Spectra

A first estimate of the rotational constants was obtained by assuming that the water molecule is bound to the nitrogen atom (N₁) of PRM in a way similar to that in pyrazine-water,¹¹ i.e., to result in a planar complex with a bent O-H \cdots N hydrogen bond (\angle NHO = 152° and $r_{\text{H}\cdots\text{N}}$ = 1.94 Å, see Figure 1). The geometries of PRM²¹ and water²² were assumed to remain unaltered in the complex. Due to the syn or anti position of the second ring nitrogen (N₃) with respect to the oxygen, and to the *zusammen* or *entgegen* configuration of the hydrogen bond and the nonbonded water hydrogen, four possible planar conformations may be anticipated for the complex. These configurations are drawn in Figure 1, where the abbreviations S, A, Z, E are used for *Syn*, *Anti*, *Zusammen*, and *Entgegen*, respectively. The spectrum was predicted to be that of a near-symmetric prolate rotor with two components of the dipole moment along the *a* and *b* inertial axes. The search for the rotational spectrum was carried out with the mm-wave spectrometer in Bologna. At the rotational temperature achieved with the free jet the strongest transitions were expected to be *R*-branch μ_b -type, with *J* ranging from 6 to 14. These were, in fact, the first transitions to be assigned, and the assignment was confirmed by subsequent observation of several higher-*J*, μ_a -type transitions. Rotational spectra of isotopomers of PRM-water with D₂O, HDO, and H₂¹⁸O were then recorded. No hyperfine structure due to the presence of the two ¹⁴N nuclear quadrupoles, or to large-amplitude water motions, was observed. Such motions are often associated with a double-minimum potential, and to ascertain if the associated splitting was present, we investigated in detail the spectrum of the normal species at higher resolution and lower rotational temperature, with the centimeter-wave, FTMW spectrometer in Warsaw. Only the hyperfine structure arising from the two ¹⁴N nuclei could be observed. The absence of any vibrational splitting suggests that the water unit is quite "rigid" in this complex. The measured frequencies of mm-wave rotational transitions are available as

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Table 1. Rotational and Centrifugal Distortion Constants and Inertial Defects for Four Different Isotopomers of PRM...H₂O

	PRM...HOH	PRM...H ¹⁸ OH	PRM...DOH	PRM...DOD
<i>A</i> /MHz	6201.229(3) ^a	6200.64(3)	6187.63(3)	6160.06(3)
<i>B</i> /MHz	1490.7754(6)	1397.10(1)	1464.15(2)	1400.635(9)
<i>C</i> /MHz	1202.4455(6)	1140.72(2)	1184.67(2)	1142.284(9)
<i>D_J</i> /kHz	0.482(5)	0.50(2)	0.49(1)	0.409(7)
<i>D_{JK}</i> /kHz	12.05(5)	11.18(7)	11.61(7)	10.79(4)
<i>D_J</i> /kHz	-10.9(1)	-10.6(5)	-10.8(4)	-9.3(4)
<i>d</i> ₁	-0.094(9)	-0.13(2)	-0.06(3)	-0.097(7)
<i>d</i> ₂	-0.061(5)	-0.040(6)	-0.03(1)	-0.036(4)
$\Delta_i = I_c - (I_a + I_b)/u\text{\AA}^2$	-0.209	-0.194	-0.240	-0.427
<i>N</i> ^b	54	29	37	43
<i>J</i> _{max}	23	16	24	25
σ^c /MHz	0.11	0.08	0.11	0.09

^a The quantity in parentheses is the standard error in units of the last digit. ^b The number of fitted transitions. ^c Standard deviation of the fit.

Table 2. Comparison of the Experimental Substitution Coordinates (Å) of the Normal Species with Values Calculated for the Four Possible Conformers^a

	exptl	calcd			
		<i>A-E</i>	<i>S-E</i>	<i>A-Z</i>	<i>S-Z</i>
<i>a</i> (O)	3.40	3.41	3.40	3.42	3.41
<i>b</i> (O)	0.09	0.07	0.06	0.03	0.04
<i>c</i> (O)	0.06	0.0	0.0	0.0	0.0
<i>a</i> (H')	2.48	2.52	2.52	2.52	2.52
<i>b</i> (H')	0.41	0.28	0.33	0.36	0.41
<i>c</i> (H')	0.13	0.0	0.0	0.0	0.0
<i>a</i> (H)	3.95 ^b	3.98	3.99	3.32	3.28
<i>b</i> (H)	0.54 ^b	0.70	0.70	0.92	0.90
<i>c</i> (H)	0.31 ^b	0.0	0.0	0.0	0.0

^a The primed hydrogen participates in the hydrogen bond. ^b Obtained from the coordinates of H in the PRM-D'OH principal system by adding the model differences between of H' in the PRM-H₂O and PRM-D'OH principal axis systems.

Supporting Information. They have been fitted with Watson's *S*-reduced Hamiltonian²³ in representation *F*. The rotational and centrifugal distortion constants determined for all isotopomers are listed in Table 1. The values for the normal species are more precise due to inclusion of hyperfine corrected central frequencies measured with the FTMW spectrometer (see the next section).

Geometry of PRM-Water

(a) Evidence from the Rotational Spectrum. The small values of the ground-state inertia defect $\Delta_i = -0.21, -0.43, -0.24,$ and $-0.19 \text{ u}\text{\AA}^2$, for the normal, D₂O, HDO, and H₂¹⁸O species, respectively, suggest planar or near-planar geometry of the complex. This is reflected by the values of the substitution, *r_s*, coordinates, obtained by applying Kraitchmann's equations²⁴ to the rotational constants of the four isotopomers. The small nonzero values of the |*c*| coordinates are interpretable as due to the large-amplitude motions of the water moiety with respect to PRM (see, for example, ref 14), and therefore compatible with zero equilibrium values. Although *r_s* coordinates are likely to be affected by these large-amplitude motions, and by the shrinkage of the O...N distance upon deuteration (Ubbelohde effect²⁵), we believe that they are sufficiently reliable for conformational assignment. They are compared in Table 2 with the values calculated for the four conformers of Figure 1 by assuming an O-H...N hydrogen bond with

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Table 3. The Nuclear Quadrupole Coupling Constants for the Two ¹⁴N Nuclei in PRM...H₂O, Compared with Those for the Pyrimidine Monomer

	PRM-W (N _a)	PRM-W (N _b)	PRM ^a
$\chi_{aa'}$ /MHz	-3.7709(29)	-1.8872(34)	-3.1007(8)
$\chi_{bb'} - \chi_{cc'}$	-2.3736(64)	-4.7756(68)	-3.6110(13)
χ_{ab}	±2.19(37)	±2.63(37)	±2.71(10)
χ_{zz}	-4.67(26)	-4.31(37)	-4.81(8)
χ_{xx}	1.59(26)	0.97(37)	1.45(8)
$\chi_{yy} (= \chi_{cc'})$	3.072(4)	3.331(4)	3.3558(7)
θ_{za} /deg	22.2(24)	42.6(3)	31.5(4) ^c
σ /kHz		1.9 ^b	

^a From ref 21. ^b The values of rotational and centrifugal distortion constants, except for Δ_K , were allowed to deviate in this fit from those in Table 1 to account more precisely for the center frequencies of the rotational transitions. ^c The angle between the \angle CNC bisector and the *a*-axis is 31.4° from the structure in ref 21.

geometrical parameters taken from pyrazine-water¹¹ ($\theta = 152^\circ$ and $r_{\text{H}\cdots\text{N}} = 1.94 \text{ \AA}$). This comparison allows the *A-Z* and *S-Z* conformers to be ruled out on the basis of large discrepancies between experimental and calculated values of |*a*| and |*b*| coordinates of the nonbonded water hydrogen, but it cannot discriminate between the *A-E* and *S-E* species.

(b) Evidence from the Hyperfine Structure due to the Two ¹⁴N Nuclei. The spectrum of the normal isotopomer of the adduct, when investigated at sub-Doppler resolution at the ca. 1 K effective kinetic temperature of the sample in the supersonic of the FTMW spectrometer, revealed only the hyperfine structure arising from the presence of two ¹⁴N quadrupolar nuclei in the pyrimidine subunit. The measured frequencies of the quadrupole splitting components are available as Supporting Information, and the quadrupole coupling constants, which result from fitting these data by using the $I = I(N_a) + I(N_b)$, $F = J + I$ coupling scheme of angular momenta and the program SPFIT written by H. M. Pickett,²⁶ are given in Table 3. Nonzero values of only two off-diagonal quadrupole tensor components, $\chi_{ab}(N_a)$ and $\chi_{ab}(N_b)$, could be fitted and confirm that the complex is planar or near-planar. The angles θ_{za} between the *a* principal axis and the *z* directions of the quadrupole tensors at N_a and N_b in the complex are 22.2(25)° and 42.6(4)°, respectively. It is expected that the directions of the field gradient axes at the nitrogen nuclei of pyrimidine are not affected by complexation so that the comparison with θ_{za} in free pyrimidine is indicative of ca. 10° rotation of the *a*-axis of the pyrimidine unit (which is parallel to the N-N axis) away from the *a*-axis of the complex. The angles from the quadrupolar analysis were built in as an additional constraint in a least-squares fit of the ground

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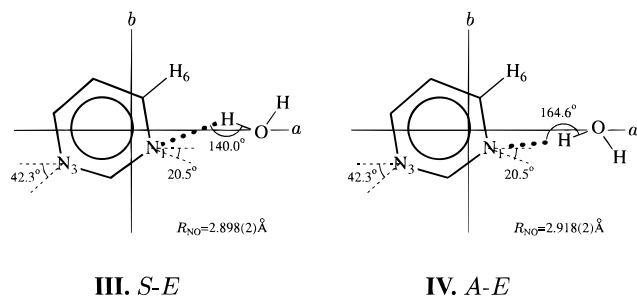
III. *S-E*IV. *A-E*

Figure 2. The r_0 geometries of PRM–water compatible with orientations of z -axes of the principal nuclear quadrupole tensors on the two nitrogen nuclei in PRM–water. Species *AE* is the observed one.

state structure of the complex. Internal coordinates were fitted directly to moments of inertia²⁷ of all four isotopomers simultaneously. Unchanged r_0 geometries for pyrimidine²¹ and water²² and collinearity of quadrupolar z -axes with the $\angle\text{CNC}$ bisector have been assumed. It was quickly found that only the *A-E* and *S-E* species gave rise to convergent solutions. Two sets of fits were possible, depending on the identification of the nitrogen nuclei N_a , N_b from the quadrupolar analysis with physical nuclei N_1 , N_3 (see Figure 1). The two solutions for $N_a \equiv N_3$, $N_b \equiv N_1$ were readily excluded on grounds of giving rise to unphysical proximity between a water and a pyrimidine hydrogen, of 1.37 and 1.05 Å for *A-E* and *S-E*, respectively. The two remaining r_0 geometries resulting from fits of *A-E* and *S-E* structures for the identification $N_a \equiv N_1$, $N_b \equiv N_3$ are reproduced in Figure 2. The two fits are of identical quality and, for the assumption of a planar geometry, the moments of inertia are fitted to an average deviation of 0.17 uÅ² with only two adjustable structural parameters, the N–O distance and $\angle\text{NHO}$. The experimental data also provide some evidence in favor of a small degree of nonplanarity since the inertial defect for PRM–D₂O is twice the value for PRM–H₂O. If nonplanarity is allowed then a somewhat better fit to the data is obtained by 15° rotation of the water unit about the hydrogen bond, so that the nonbonded hydrogen is ca. 0.2 Å above the pyrimidine plane.

Although the two geometries in Figure 2 are equally consistent with the observed rotational constants it is now possible to discriminate between them on steric grounds. In the *S-E* geometry the distance between the pyrimidine hydrogen H_6 and the hydrogen bond hydrogen is 1.89 Å, which is too low. Although the sum of Pauling's van der Waals radii for two hydrogens is 2.4 Å, H–H distances down to ca. 2.1 Å might be acceptable, but not below. In the *A-E* geometry $d(H_6H) = 2.28$ Å, which is reasonable. The hydrogen bond N···H distances are 1.98 Å for *A-E* and 2.09 Å for *S-E*, and the former is much closer to 1.94 Å determined for pyrazine–H₂O. In addition, as found below, the binding energy for this complex is not particularly low, and on this basis the *A-E* geometry, which has a smaller bend in the hydrogen bond, would again be preferred.

(c) Evidence from *ab Initio* Calculations. Although *ab initio* calculations for PRM–W have been reported,¹⁵ their emphasis was on vibrational frequencies and details of the structure have not been published, except that an N···HO bonded, *A-E* type configuration was determined. Spectroscopic results above suggest that relative orientation of the molecular planes of water and of pyrimidine is a key coordinate in defining the equilibrium geometry of PRM–W, and we have decided to

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Table 4. The Calculated Dimerization Energies and Relative Energies of Structures of PRM–H₂O Obtained from *ab Initio* Calculations and from the Electrostatic Model

	$-\Delta E^a$		$\Delta E_1^b/\text{cm}^{-1}$	
	kJ mol^{-1}	cm^{-1}	$\varphi = 0^\circ$ (<i>A-E</i>)	$\varphi = 180^\circ$ (<i>S-E</i>)
3-21G*	43.8	3665	338	0 ($\varphi = 81$)
6-31G**	22.1	1846	129	0 ($\varphi = 75$)
6-31G+***	20.9	1750	4	0 ($\varphi = 16$)
electrostatic model	17.8	1488	71	0 ($\varphi = 77$)
6-31G**–BSSE	18.6	1552	0	76 ($\varphi = 75$)
6-31G**+MP2– BSSE	21.4	1790	0	117 ($\varphi = 75$)

^a The dimerization energy $\Delta E = E(\text{PRM–H}_2\text{O}) - E(\text{PRM}) - E(\text{H}_2\text{O})$. For the electrostatic model the quantity $-E_{es}/2$ is tabulated from approximation to a Lennard-Jones potential in which the energy at minimum equals half the attractive term. ^b The energy relative to the global minimum for this calculation. ^c The angle φ defining the nonplanar configuration is the angle subtended in the bc inertial plane between the nonbonded HO bond of H₂O and the plane of pyrimidine.

investigate this in more detail. The range of possible geometries can be characterized by a rotation angle φ describing the rotation of the H₂O unit relative to the plane of pyrimidine (see Table 4). The planar *A-E* structure is defined to correspond to $\varphi = 0^\circ$. We have carried out three sets of optimizations: for an unconstrained *C_i* geometry and for two *C_s* geometries, *A-E* and *S-E* of Figure 1. Full geometry optimizations were carried out at the SCF level with three basis sets ranging from 3-21G* through 6-31G**, to 6-31G+*** of ref 15, by using the package GAMESS.²⁸ The results are summarized in Table 4. The 3-21G* basis is known to yield poor energies, but serves to illustrate how the calculation prefers a near-perpendicular pyrimidine–H₂O orientation, up to and inclusive of the 6-31G** basis. Yet on extending the basis up to the 6-31G+*** level the predicted global minimum is near planar, at $\varphi = 16^\circ$. The SCF results are also compared with a geometry optimization carried out with the electrostatic model of Buckingham and Fowler.²⁹ This model has been found to accurately reproduce angular geometries of many hydrogen bonded clusters and uses distributed multipole (DMA) parametrization of the *ab initio* electron distribution of the monomer molecules and minimizes the electrostatic interaction of the two molecules counterbalanced by a hard core repulsive term. Since the electrostatic term is the major contributor to the hydrogen bond energy, the electrostatic model yields, at a much lower computational cost, results which are comparable with supermolecule calculations. This is confirmed for PRM–W: the electrostatic results obtained from DMA's for water and pyrimidine evaluated also at the 6-31G** level and taken up to the octopole level are very similar to those of the 6-31G** supermolecule calculation. In all calculations, the *S-E* geometry is found to be the least stable. Nevertheless, since at the higher levels of calculation the relative stabilities between two lowest energy, the *A-E* and the nonplanar, geometries are at the 1 kJ mol^{−1} level, they are sufficiently small to be sensitive to the several known corrections that have to be applied to make the results more precise. The first such correction concerns the basis set superposition error (BSSE) that is due to a larger number of basis functions being available in a supermolecule calculation to define monomer energies than

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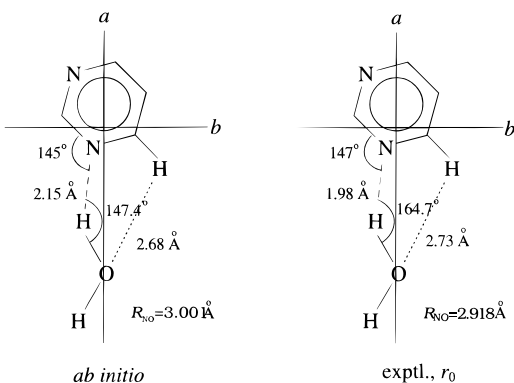


Figure 3. Comparison of the *ab initio* and experimental geometries for the observed conformer (*AE*) of PRM–water. The pyrimidine and the water O–H bond that participates in the hydrogen bond are coplanar, although the nonbonded hydrogen of H₂O may be up to 0.4 Å above this plane.

in a monomer calculation at the same basis. We have used the counterpoise method of Boys and Bernardi³⁰ and decided to correct the results from the better known 6-31G** basis. This basis contains considerably fewer diffuse functions than 6-31G+**, so that E_{BSSE} is expected to be smaller in magnitude and more reliable. It can be seen from Table 4 that the BSSE correction exchanges the relative energies of the planar *A-E* and the near-perpendicular geometries almost exactly. The next step is to estimate the magnitude of the dispersive contribution to the interaction energy, which has been made by calculating the second-order Moller–Plesset (MP2) correlation correction, at the level of the BSSE correction. Addition of the MP2 energy has the effect of stabilizing the *A-E* geometry further in relation to the near-perpendicular form. In all cases the *S-E* geometry is the least stable, which provides support for previous preference of *A-E* out of the pair of *A-E*, *S-E*. Thus the corrected 6-31G** and the uncorrected 6-31G+** results support the experimental conclusion that the geometry of PRM–W is of *A-E* symmetry with the possibility of effective near-planar geometry due to a flattened potential surface, or even a small barrier near $\varphi = 0^\circ$. In light of the above, the electrostatic model meets with only partial success since it correctly predicts the type of hydrogen bond and its energy, but has not been able to deal successfully with fine details of the energetics arising on rotation of H₂O relative to the plane of pyrimidine. The present study has also revealed that computational determination of reliable intermolecular potential for PRM–W along the φ coordinate will require a dedicated *ab initio* study at a substantially higher level of accuracy than 1 kJ mol⁻¹.

Both experimental and computational evidence leads to the conclusion that PRM–W has planar or nearly planar *A-E* type geometry from Figure 1. The experimental r_0 geometry and the 6-31G** *ab initio* geometries are compared in Figure 3. Although there still remains some uncertainty concerning whether the nonbonded hydrogen of H₂O is in the pyrimidine plane or not, the values of the parameters shown in Figure 3 are insensitive to this. It can be seen that there is agreement between experiment and calculation concerning several key features of the geometry of the adduct. It is clear that the N···H–O hydrogen bond has an appreciable bend from linearity and that the N···H axis is bent 23–25° away from the $\angle\text{CNC}$ bisector. Both of these distortions serve to bring the nuclei in the bonded HO bond into van der Waals proximity with H₆ of the pyrimidine nucleus, and allow an increase in the energy of

dispersive interaction between pyrimidine and water. This type of behavior, in which interaction peripheral to the hydrogen bond plays a role in determining the geometry of the adduct, has been observed for several adducts and has been discussed in the results for methylenecyclopropane···HCl.³¹

Internal Motions

The three translational and the three rotational degrees of freedom of the isolated water molecule are replaced by six low energy vibrational modes upon formation of the complex. One of these motions is the stretching motion between the two constituent molecules, while the remaining modes can be classified as two intermolecular bends and three internal rotations or torsions of the water moiety.

The intermolecular stretch is sufficiently well isolated from the other low-frequency motions so that meaningful hydrogen bond stretching constants are obtained by approximating the complex to a diatomic. Enhanced formulas of this type have been developed by Millen for linear and symmetric top complexes³² and by Read et al.³³ for asymmetric top complexes in which the stretching coordinate is near-parallel to the inertial *a*-axis. This condition is satisfied for PRM–W, so that the equation

$$k_s = 16\pi^4(\mu_A R_{\text{CM}})^2 [4B_A^4 + 4C_A^4 - (B_A - C_A)^2(B_A + C_A)^2] / (hD_J) \quad (1)$$

can be used to derive the hydrogen bond stretching force constant k_s . The subscript A denotes a adduct quantity, μ_A is the pseudodiatomic reduced mass, R_{CM} is the distance between the centers of mass of the monomers (4.16 Å for PRM–W), and D_J is the centrifugal distortion constant. For PRM–W $k_s = 13.8 \text{ Nm}^{-1}$ and corresponds to a stretching frequency of 126 cm⁻¹. This is slightly higher than $k_s = 12.5 \text{ Nm}^{-1}$ for H₂O···HCl,³⁴ and is consistent with somewhat lower dimerization energy $\Delta E = 20 \text{ kJ mol}^{-1}$ calculated for that dimer.³⁵ The k_s comparison with pyrazine–H₂O and also with (H₂O)₂ cannot be made reliably since in both cases the value of D_J is perturbed by large-amplitude motions. Nevertheless, the calculated dimerization energy for (H₂O)₂ of 21.1 kJ/mol³⁶ is very close to our best value of 21.4 kJ/mol for PRM–W.

The low-frequency bending and torsional motions present too many internal coordinates for a unique determination. Nevertheless, it is known that if such modes are associated with highly anharmonic potentials then this is reflected in anomalously high values of centrifugal distortion constants, in particular those for D_{JK} and D_K .³⁷ This does not appear to be the case for PRM–W, and test calculations have also shown that the observed values of all five quartic constants are readily reproduced by a harmonic force field based on reasonable assumptions. This type of calculation is useful in identifying the magnitude of vibration–rotation contributions to measured moments of inertia and the corrected, average moments of inertia, I^* ,³⁸ are a more accurate representation of the equilibrium geometry of the molecule. The average inertial defect calculated for PRM–W

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is $\Delta_1^* = \Delta_1^0 - 0.35 \text{ u } \text{\AA}^2$, and this result is rather insensitive to details of the assumed force field. The magnitude of the correction is consistent with previous observations that the ground-state inertia defect carries a positive vibration-rotation contribution relative to Δ_1^* , which ranges from $3 \text{ u } \text{\AA}^2$ for adducts with Ar to several tenths of $\text{u } \text{\AA}^2$ for hydrogen bonded adducts.³⁹ Inclusion of this correction in the structural fit leads to a further improvement in the quality of the fit and rotation of the H_2O by ca. 30° out of the pyrimidine plane, so that the nonbonded hydrogen is ca. 0.4 \AA above this plane. However, the implication of a double-minimum potential with minima at $\varphi = \pm 30^\circ$ has to be confronted with expectation if there is an appreciable central barrier, then two states should be observed, as in pyrazine- H_2O . The present observation of only a single state indicates that the central barrier, if present, is small and well below the vibrational ground state of the complex. The most economical conclusion from both experiment and calculation is that the molecular potential for rotation of H_2O about the hydrogen bond axis is very shallow for considerable angular distance away from the planar *A-E* geometry, and that there is some possibility of a slightly nonplanar equilibrium geometry.

Comparison with Previous Aromatic Molecule-Water Investigations and Conclusions. Comparison of our results for PRM- H_2O with those for known complexes of water with other aromatic molecules, benzene-water,^{4,5} pyrazine-water,¹¹ and pyrrole-water,⁷ shows how hydration can be achieved in markedly different ways. Three different hydrogen bond

arrangements are found: $\pi \cdots \text{H}-\text{O}$ in benzene-water, $\text{N}-\text{H} \cdots \text{O}$ in pyrrole-water, and $\text{N} \cdots \text{H}-\text{O}$ in pyrazine-water and PRM-water. Furthermore, the two last cases differ considerably in their spectroscopic manifestations of large-amplitude motions of water relative to the ring and therefore in shapes of their potential energy surfaces near the minimum. The double-minimum potential in pyrazine-water generates a vibrational splitting of the ground state, with μ_b -type interstate transitions, while in PRM-water the ground state is located either in the single global minimum or well above a small barrier between two possible nonplanar minima. These differences must have played a role in inducing nature to choose a pyrimidine type unit for a common base in biological systems. We believe that the kind of interaction we have studied is one of the most common in biology and that our results can provide a firm experimental starting model for the interpretation of similar linkages in more complicated systems occurring in nature.

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Supporting Information Available: Tables of measured transition frequencies in the millimeter-wave rotational spectrum of PRM-water and assignments, frequencies, and observed-calculated differences of the hyperfine components for the parent isotopomer of PRM-water (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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