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Theoretical Study of the Interaction Between 2-Aminopyridine and 2-Aminopyrazine and Water[*]

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This work deals with a theoretical study of the interaction between one water molecule with 2-aminopyridine (2-NH_2PYR) and 2-aminopyrazine (2-NH_2PYZ). The optimized geometries, harmonic vibrational frequencies, binding energies, proton affinities of the heterocyclic nitrogen atom and the deprotonation enthalpies of the NH bonds are calculated by the DFT/B3LYP functional combined with the 6-31+G(d,p) basis set. The two complexes are cyclic. Complex formation results in a marked decrease of the pyramidal character of the amino group. The binding energies with water are –27.8 kJ mol^{-1} (2-NH_2PYR) and –25.2 kJ mol^{-1} (2-NH_2PYZ). The comparison with complexes involving nucleobases and one water molecule indicates that, in contrast with the interaction involving the carbonyl group, there is no correlation between the binding energies and the acidities and basicities of the sites involved in the interaction. The results are discussed in terms of marked angular differences of the hydrogen bonds forming the closed ring.

Key words: 2-aminopyridine, 2-aminopyrazine, interaction with water, B3LYP/6-31+G(d,p) calculations

In recent years, much attention has been paid to the geometry of the NH_2 group in aromatic derivatives together with the influence of the interaction with water on the pyramidal character of this group. More specifically, the interaction between nucleobases such as cytosine, adenine and guanine and water has been the subject of several recent investigations [1–8]. In the present work, the interaction between 2-aminopyridine (2-NH_2PYR) and 2-aminopyrazine (2-NH_2PYZ) and water is investigated theoretically by the density functional theory (DFT). In both molecules, the NH_2 group is in ortho position with respect to the nitrogen atom of the heteroaromatic ring and in this respect the molecules can mimic the behaviour of nucleobases such as cytosine or adenine. It must be noticed that no experimental data are available for these complexes. From a theoretical point of view, the interaction between 2-NH_2PYR and water has been investigated at a low level of theory (SCF calculations with the STO-3G basis set) [9].

This work is arranged as follows. In the first part, we discuss the optimized geometry of the complexes. The second part deals with the vibrational frequencies and in the last part, we report the proton affinities of the heterocyclic nitrogen atom and the deprotonation enthalpies of the NH bonds of the 2-NH_2PYR and 2-NH_2PYZ

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[*] Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

molecules. The binding energies of the two molecules with water are compared with literature data for the complexes between nucleobases and water.

COMPUTATIONAL METHODS

The structures of isolated 2-NH_2PYR and 2-NH_2PYZ were fully optimized by the density three-parameter hybrid model (DFT/B3LYP) [10-12] using the 6-31+G(d,p) basis set. It is known from literature that the use of the 6-31++G(d,p) basis set affects only slightly the binding energies and vibrational frequencies of the complexes as compared to 6-31+G(d,p) basis set [1–8]. This method also provides reliable data related to the acidities of nucleobases [13]. The harmonic frequencies and infrared intensities were calculated at the same level of theory. The binding energies of 2-NH_2PYR and 2-NH_2PYZ with one water molecule were calculated as the differences of the energy of the complex and the energy of the separated monomers. (In general, energy differences due to the use of the 6-31++G(d,p) basis set were found to be very small [6]). The counterpoise procedure of Boys and Bernardi [14] was applied to correct for the basis set superposition error (BSSE). The zero-point vibrational energy (ZPE) correction has also been included. All the calculations were carried out using the GAUSSIAN 94 package [15].

RESULTS AND DISCUSSION

Structure of isolated 2-NH_2-PYR and 2-NH_2PYZ and their water complexes. Tables 1 and 2 contain selected geometrical parameters in the isolated components and their complexes with one water molecule. The structure of 2-NH_2PYR has been investigated by *ab initio* methods and the ring geometry was found to be quite insensitive to the level of the calculations [16]. All the theoretical methods reveal a marked pyramidal character of the amino group, the sum of the angles around the nitrogen of the amino group being equal to 343.5° (HF/6-31G(d), 339.6° (MP2/6-31G(d) and 340.7° (MP2/6-311G(2df, p) [7].

Table 1. Selected geometrical parameters in isolated 2-NH_2PYR, H_2O and 2-NH_2PYR·H_2O (distances in Å, angles in degrees) and bond length or angle differences (Δ).

	2-NH_2PYR[a]	2-NH_2PYR·H_2O	Δ
rN7H13	1.0107	1.0158	+0.0051
rN7H12	1.0089	1.0064	–0.0025
rC4N7	1.3836 (1.351)	1.3680	–0.0156
rC4N5	1.3420 (1.345)	1.3497	+0.0077
rC6N5	1.3402 (1.340)	1.3426	+0.0024
∠H12N7H13	115.3 (117.2)	118.5	+3.2
∠C4N7H12	118.0 (120.2)	119.6	+1.6
∠C4N7H13	114.8 (121.2)	118.5	+3.7
τC3C4N7H12	25.1	13.0	–12.1
τN5C4N7H13	–16.0	–9.7	+6.3
α	17.5	3.4	
β	9.1	3.3	

	H_2O	2-NH_2PYR·H_2O	Δ
rO_wH_w	0.9650	0.9864	+0.0214
rO_wH_w’	0.9650	0.9641	–0.0009
∠$H_wO_wH_w$’	105.7	107.0	+1.3

	Intermolecular parameters
H_w...N5	1.8926
H13...O_w	2.0851
∠ N7H_wO_w	143.4

[a] The experimental values [17] are given in parentheses.

Table 2. Selected geometrical parameters for isolated 2-NH_2PYZ and 2-NH_2PYZ·H_2O (distances in Å, angles in degrees) and bond length or angle differences (Δ).

	2-NH_2PYZ	2-NH_2PYZ·H_2O	Δ
rN7H12	1.0104	1.0173	+0.0069
rN7H11	1.0087	1.0071	–0.0016
rC4N7	1.3772	1.3634	–0.0138
rC4N5	1.3390	1.3463	+0.0073
rC6N5	1.3399	1.3416	+0.0017
∠ H11N7H12	115.9	118.3	+2.4
∠C4N7H11	118.6	119.5	+0.9
∠C4N7H12	115.7	188.8	+3.1
τC3C4N7H11	22.4	12.9	–9.5
τ N5C4N7H12	–15.3	–9.5	+5.8
α	9.8	3.4	
β	7.1	3.4	

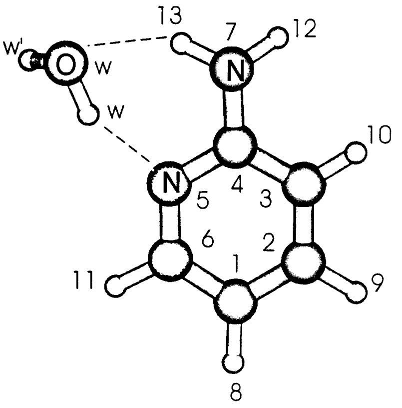
	H_2O	2-NH_2PYZ·H_2O	Δ
rO_wH_w	0.9650	0.9826	+0.0176
rO_wH_w’	0.9650	0.9642	–0.0008
∠ $H_wO_wH_w$’	105.7	107.2	+1.5

	Intermolecular parameters
H_w…N5	1.9042
H12…O_w	2.0603
∠N7H_wO_w	143.5

Our value of 348.1° is in relative good agreement with these values. It should be noticed that the structure of crystalline 2-NH_2PYR has been determined by X-ray diffraction [17]. Selected geometrical parameters in the gas phase and in the crystalline state are listed in Table 1. The data show that the C4N7 bond is shorter by *ca* 0.03 Å in the solid state than in the isolated molecule. Further, the sum of the angles around the N atom (358.6°), which indicates a nearly perfect sp^2 hybridization, is markedly larger in the crystalline state than in the isolated molecule. This difference can be accounted for by the existence of N7H13…N5 hydrogen bonds in the crystalline state. The formation of this intermolecular hydrogen bond results in an increase of the electronic delocalization in the C4N7 bond and a decrease by 0.034 Å of the corresponding bond length.

As illustrated in Figures 1 and 2, the 2-NH_2PYR·H_2O and 2-NH_2PYZ·H_2O complexes are cyclic and are stabilized by two distorted OH…N and NH…O hydrogen bonds.

Let us first analyze the influence of the complexation with one water molecule on the pyramidal character of the amino group. As discussed in recent works [1–8,16,18], there are two structural sources of nonplanarity. The nonplanarity of the first type is related to the partial sp^3 hybridization of the amino group and can be estimated as the deviation of the sum of the angles around the nitrogen atom from 360° (α in Tables 1 and 2). The nonplanarity of the second type is related to the interaction of one of the H atoms of the amino group with the closest H atom and can be estimated from the difference of the absolute values of the corresponding dihedral angles (β in Tables 1

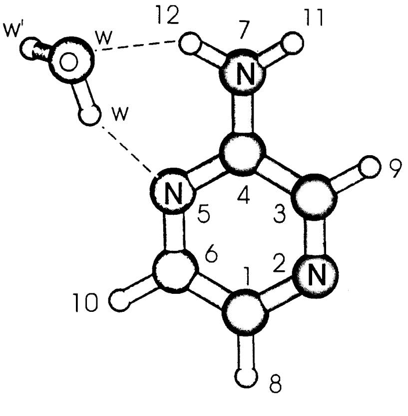


E_T = -380.125546 a.u.

E_{HB} = -39.3 kJ/mol

E_{HB} (with ZPE and BSSE) = -27.8 kJ/mol

Figure 1. B3LYP/6-31+G(d,p) optimized structure of the 2-NH_2PYR·H_2O complex.



E_T = -396.156378 a.u.

E_{HB} = -36.7 kJ/mol

E_{HB} (with ZPE and BSSE) = -25.2 kJ/mol

Figure 2. B3LYP/6-31+G(d,p) optimized structure of the 2-NH_2PYZ·H_2O complex.

and 2). In the two isolated molecules, both effects are operating, the pyramidal character of the amino group being somewhat larger for 2-NH_2PYR than for 2-NH_2PYZ. Complex formation with water induces a marked decrease of the pyramidal character of the amino group; in both complexes, the α and β values equal to 3.3–3.4° become smaller than in the isolated molecules. The nonplanarity of the first type seems to be the determinant factor, at least in the present systems. Indeed, the distance between the nonbonded atoms H10 and H12, equal to 2.502 Å in isolated 2-NH_2PYR, decreases to 2.471 Å in the water complex. The same trend is predicted for in 2-NH_2PYZ, where the distance between the nonbonded atoms H9 and H11 is equal to 2.511 Å in the free molecule and 2.479 Å in the water complex. Further, a comparison with previously studied systems (isolated guanine, adenine and cytosine and their 1-1 water complexes) [6,7] indicates a correlation between the C4N7 distances and the α values. This correlation is illustrated in Figure 3. No correlation could be found between the C4N7 distances and the β values, suggesting again that the nonplanarity of the first type predominates in the present systems.

As indicated in Tables 1 and 2, complex formation with water results in a small lengthening of the bonded NH group, by 0.0051 and 0.0069 Å and a small contraction of the nonbonded NH group, by 0.0025 and 0.0016 Å. From these data, an anticooperative effect can be predicted for the nonbonded NH group. This effect has been demonstrated experimentally by infrared spectroscopy in ortho-substituted anilines. In these systems, the weakening of the intramolecular NH...O hydrogen

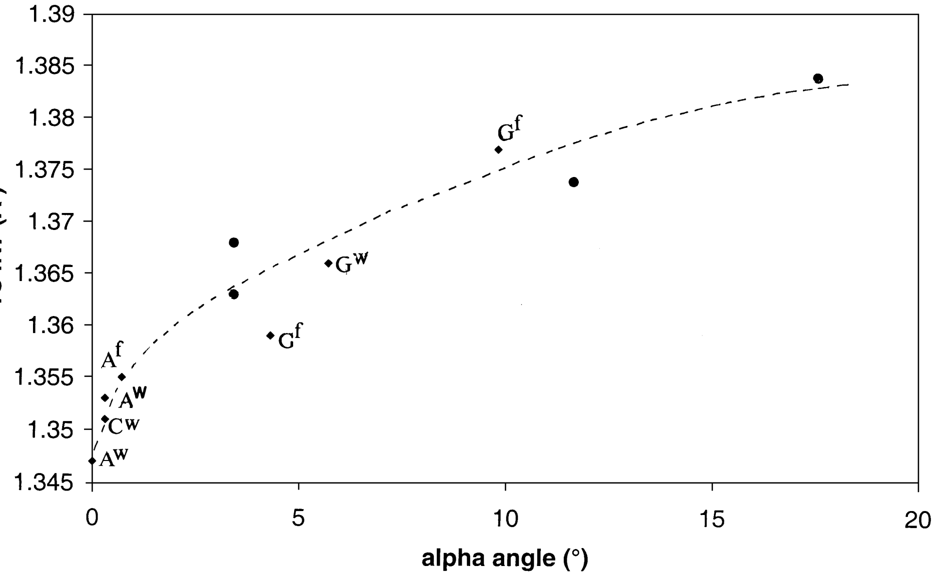


Figure 3. rC4N7 (Å) as a function of α (degrees). A, C and G refer to isolated adenine, cytosine, guanine and A^w, C^w and G^w to their cyclic water complexes formed on the nitrogen atom of the heterocyclic ring and NH group (indicated by ◆(ref. 6-8). The data of the present work are indicated by •.

bond under the influence of the intermolecular NH…B bond has been found to occur [19]. The same remark also holds for the nonbonded O_wH_w' group of water, which undergoes a small contraction in the two complexes. Our results also demonstrate that complex formation induces a small decrease of the C4N7 distance and small changes of the intramolecular distances in the heteroaromatic ring, the largest perturbations occurring in the C4N5 bonds involved in the formation of the six-membered ring [20].

Vibrational frequencies. The harmonic vibrational frequencies and infrared intensities of selected vibrational modes in the isolated molecules and their water complexes are listed in Tables 3 and 4 [20]. Several vibrational modes, namely the νCH vibrations calculated to occur between 3215 and 3150 cm^{-1}, the aromatic ring vibrations 8a, 8b, 19a and 19b, predicted between 1620 and 1460 cm^{-1} and the γCH vibrations calculated between 995 and 750 cm^{-1} show small sensitivity to complex formation and therefore are not listed in these tables. In the isolated 2-NH_2PYR and 2-NH_2PYZ molecules, the rNH_2 vibration predicted around 1055 cm^{-1} with a very weak infrared intensity is not mixed with other modes. In contrast, the ωNH_2 and τNH_2 vibrations calculated between 600 and 200 cm^{-1} appear to be coupled with the aromatic ring out-of-plane vibrations. In 2-NH_2PYR and 2-NH_2PYZ, the main component of the τNH_2 vibration is calculated at 480 cm^{-1} and 451 cm^{-1}, respectively. It must be mentioned that in cytosine several vibrational modes predicted between 640 and 400 cm^{-1} are mixed with the τNH_2 vibration [21,22]. The inversion mode of the NH_2 group in cytosine is predicted at 230 cm^{-1} by B3LYP calculations at the 6-31G(d,p) level [23]. No clear inversion modes in the isolated 2-NH_2PYR and 2-NH_2PYZ molecules could be evidenced by the present calculations.

Table 3. Selected harmonic vibrational frequencies (cm^{-1}) and infrared intensities (km mol^{-1}, in parentheses) in isolated 2-NH_2PYR and in NH_2-PYR$\cdot$ H_2O and corresponding frequency shifts.

2-NH_2PYR	2-NH_2PYR$\cdot H_2O$	assignment	$\Delta\nu$
3712 (32)	3719 (77)	$\nu^{as}NH_2$	+7
3588 (40)	3524 (482)	$\nu^{s}NH_2 + \nu^{s}H_2O$	–64
1657 (335)	1678 (257)	δNH_2 + AR (8a)	+21
1633 (9)	1658 (128)	AR (8a) + δNH_2	+25
1341 (50)	1363 (6)	νC4C7	+22
1054 (2)	1064 (2)	rNH_2	+10
1000 (6)	1006 (14)	Ring breathing	+6
545 (30)		γCH9 + τNH_2	
	526 (32)	γCH9	
480 (233)	616 (55)	τNH_2	
403 (17)	429 (47)	{ ωNH_2 + out-of-plane ring modes + τNH_2	
368 (63)	403 (40)		
201 (8)	268 (195)		
H_2O	2-NH_2PYR		
3931 (66)	3887 (76)	$\nu^{as}H_2O$	–43
3809 (10)	3421 (610)	$\nu^{s}H_2O + \nu^{s}NH_2$	–378
1603 (92)	1628 (80)	δH_2O	+25
	790 (206)	ωH_2O	

ν = Stretching, δ = in-plane bending, r = rocking, τ = twisting, ω = wagging, AR = aromatic ring vibration.

Table 4. Selected harmonic vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}, in parentheses) in isolated 2-NH_2PYZ and in the 2-NH_2PYZ·H_2O complex and corresponding frequency shifts.[a]

2-NH_2PYZ	2-NH_2PYZ·H_2O	assignment	$\Delta\nu$
3718 (38)	3709 (82)	$\nu^{as}NH_2$	–8
3592 (51)	3482 (18)	$\nu^{s}NH_2 + \nu^{s}H_2O$	–110
1650 (253)	1673 (194)	δNH_2	+23
1620 (8)		AR(8a) + δNH_2	
	1620 (67)	AR (8a) + δH_2O	0
1351 (54)	1367 (30)	νC4N7 + γC5H9	+16
1055 (11)	1073 (12)	rNH_2	+18
1017 (21)	1020 (33)	Ring breathing	+3
583 (3)	585 (12)	{$\tau NH_2 + \omega NH_2 +$	
451 (184)	628 (111)	out-of-plane ring modes	
396 (42)	419 (25)		
360 (87)	301 (214)		
H_2O	2-NH_2PYZ·H_2O		
3931 (66)	3890 (84)	$\nu^{as}H_2O$	–41
3809 (10)	3524 (894)	$\nu^{s}H_2O + \nu^{s}NH_2$	–275
1603 (92)	1637 (104)	δH_2O	+34
	740 (165)	ωH_2O	

[a] Same remarks as below Table 3.

As indicated by Tables 3 and 4, the $\nu^{s}NH_2$ vibration of both complexes is shifted to lower frequencies as compared to the isolated molecules. We have shown in a previous work [6] that the average of the frequencies of the $\nu^{as}NH_2$ and $\nu^{s}NH_2$ vibrations can be related to the pyramidal character of the NH_2 group. Among the nucleobases, adenine has the lower pyramidal character ($\alpha = 0.7°$) and the average of the aforementioned vibrations is 3686 cm^{-1} [6]. We failed to obtain for the free molecules and their complexes investigated in the present work a correlation between the average frequencies and the α angle. This can be accounted by a strong mixing of the $\nu^{s}NH_2$ and $\nu^{s}OH$ vibrations. As indicated in Table 4, the infrared intensity of the coupled $\nu^{s}NH_2$ vibration decreases from 51 to 18 km mol^{-1} and the infrared intensity of the $\nu^{s}H_2O$ vibration increases from 10 to 894 km mol^{-1} when going from isolated 2-NH_2PYR, H_2O molecules to their complexes with water. These results show that some intensity is borrowed from the $\nu^{s}NH_2$ to the $\nu^{s}H_2O$ vibration. This coupling is smaller in the 2-NH_2PYR·H_2O system than in the 2-NH_2PYZ·H_2O one and in this case, the infrared intensities of both the $\nu^{s}NH_2$ and $\nu^{s}H_2O$ vibrations increase upon complex formation.

In both complexes, the rNH_2 vibration undergoes a small blue shift of 10 and 18 cm^{-1}, respectively.

The interaction with water perturbs both the ωNH_2 and τNH_2 modes. It is worth mentioning that in the 2-NH_2PYZ·H_2O complex , the mode predicted at 301 cm^{-1} with an infrared intensity of 214 km mol^{-1} corresponds to an almost pure inversion mode of the NH_2 group.

Binding energies, protonation and deprotonation enthalpies. Table 5 contains the binding energies (E_{HB}) of one water molecule complexed with 2-NH_2PYR and 2-NH_2PYZ. This table also lists the binding energies of water complexed with several nucleobases, where water is interacting with the nitrogen atom of the heterocycle and with the NH bond. These complexes can be compared with the present ones because the same functional groups are involved in the interaction with water. Table 5 also contains the proton affinity (PA) of the heterocyclic nitrogen atom and the deprotonation enthalpy (DPE) of the NH bond interacting with water. It is worth noticing that the calculated PA value of the N5 atom (935.4 kJ mol^{-1}) and the DPE value of the NH bond (1517.1 kJ mol^{-1}) of free 2-NH_2PYR are both in very good agreement with the experimental values, which are equal to 936.4 kJ mol^{-1} [24] and 1516 kJ mol^{-1} [25], respectively. This result justifies our computational method and level. It must be mentioned that the larger PA of the N atom in 2-NH_2PYR than in 2-NH_2PYZ is in line with the larger elongation of the O_wH_w bond in the O_wH_w...N hydrogen bond in the 2-NH_2PYR · H_2O complex. The larger acidity of the NH group in 2-NH_2PYR results in a larger elongation of the NH bond in the NH...O_w hydrogen bond formed by this molecule.

Table 5. Binding energies (including ZPE and BSSE), PA, DPE (in kJ mol^{-1}), angular parameters (in degrees) for the complexes between one water molecule and 2-NH_2PYR, 2-NH_2PYZ, cytosine, adenine and guanine.

Water complex	E_{HB}	PA	DPE	∠ NH...O	τNCNH or τCCNH
2-NH_2PYR	–27.8	935.4	1517.1	143.4	–9.7
2-NH_2PYZ	–25.2	892.2	1462.3	143.5	–9.5
Cytosine (B)[a]	–34.8	922.1	1481.8	145.0	–4.0
Adenine (B)[b]	–29.8	909.6	1486.0	161.3	–1.7
Adenine (B)[b]	–26.8	943.8	1388.5	142.4	0.7
Guanine (B)[b]	–25.9	887.4	1407.4	133.2	–
Guanine (C)[b]	–25.1	887.4	1435.0	148.7	–8.3

[a]From [7]. [b]From [6]. The B and C complexes are formed on one of the N atom of the heterocyclic ring and one of the NH bond of the nucleobase.

Several correlations have been established between the binding energies, the formation constants and the frequency shifts of the νOH vibration of hydrogen-bonded complexes involving pyridine derivatives and hydroxylic proton donors [26–29]. More specifically, the binding energy of water with 4-NH_2PYR (PA = 962 kJ mol^{-1}), calculated at the MP2/6-31++G(d,p) level, is equal to –21.2 kJ mol^{-1} [28] . In this complex, the O_wH_w...N hydrogen bond formed at the nitrogen atom of the heterocyclic ring is only slightly nonlinear. The larger binding energy calculated for the less basic 2-NH_2PYR molecule results from the formation of a cyclic dimer, where two bent hydrogen bonds are present.

We have shown in our previous works [6,7] that the interaction energies of complexes formed between one water molecule and uracil, thymine and cytosine depend on both the PA and the DPE of the bonds involved in complex formation. We have obtained the following exponential expression:

$$E_{HB} = a\ e^{-b(cDPE - PA)} \text{ where } c > 1$$

Our comparison was restricted to cyclic dimers, where the C=O bond is acting as a proton acceptor and the NH bond as a proton donor. The six-membered rings formed in this way are nearly planar and the NH...O angles are almost constant, taking values between 134° and 150°. It is worth noticing that a similar equation containing two additive exponential terms has been used recently for double proton transfer reactions [30]. We failed to find a similar expression for cyclic hydrogen bonds involving a heterocyclic nitrogen atom and a NH group. The mean reason of this contrasting behaviour may be accounted for by the fact that the angular parameters vary within a broad range. As indicated in Table 5, the NH...O angles comprise between 133° to 161° and the torsional angles τNCNH or τCCNH vary within the limits of –9.7° to 0°.

CONCLUSIONS

The present work reports the results of a theoretical study carried out at the B3LYP/6-31+G(d,p) level on the interaction between 2-NH_2PYR and 2-NH_2PYZ with water. The most stable complexes are cyclic with two bent NH...O and OH...N hydrogen bonds. The hydrogen bonds are of medium strength, the binding energies do not differ markedly, being equal to –27.8 kJ mol^{-1} (2-NH_2PYR$\cdot H_2O$) and –25.2 kJ mol^{-1} (2-NH_2PYZ$\cdot H_2O$). This can be accounted for by the fact that 2-NH_2PYR is a better proton acceptor than 2-NH_2PYZ and 2-NH_2PYZ is a better proton donor than 2-NH_2PYR. Comparison with the interaction between the nucleobases cytosine, adenine, guanine and water, where closed NH...OH...N hydrogen bonds are also formed, shows that there is no relation between the binding energies and the acidity/basicity of the sites involved in the interaction. This may be due marked difference in the angular parameters in the closed dimers.

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