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Theoretical Investigation of the Interaction between 2-Pyridone/2-Hydroxypyridine and Ammonia

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The structures and harmonic vibrational frequencies of the closed complexes 2-pyridone−NH_3 (2PY−NH_3), 2-hydroxypyridine−NH_3 (2HP−NH_3), 2-pyridone−$(NH_3)_2$ (2PY−$(NH_3)_2$), and 2-hydroxypyridine−$(NH_3)_2$ (2HP−$(NH_3)_2$) were studied using the density functional theory (DFT). The final energies of each complex were obtained using the B3-LYP and MP2 methods. The NH_3 molecule is both a proton donor and a proton acceptor in the 2PY−NH_3 and 2HP−NH_3 complexes, while in the 2PY−$(NH_3)_2$ and 2HP−$(NH_3)_2$ systems, the ammonia dimer acts both as a proton donor and a proton acceptor. Comparison is made between the theoretical results and recent experimental results for the 2PY−NH_3 and 2PY−$(NH_3)_2$ complexes. In the heterotrimer complexes, the cooperative effects are substantial and this is reflected by the intermolecular distance of the ammonia dimer, by the elongation of the NH bond length, by the frequency shift of the ν(NH) mode, and by the additive interaction energy.

Introduction

Numerous studies on the tautomerization of 2-pyridone/2-hydroxypyridine (2PY/2HP) have been performed, because this process plays an important role in the mutation of DNA.[1,2] A variety of experimental measurements[3−7] has indicated that the free energy difference between the 2HP and the 2PY forms is 2−4 kJ/mol in favor of the hydroxy form. Most of the theoretical methods[8−12] used so far have supported this result. The tautomeric equilibrium depends on the environment surrounding the molecule.[13] The hydrogen bonding of 2PY/2HP with one or two ammonia molecules is studied in this work using DFT/B3-LYP/6-31++G** and MP2//B3-LYP/6-31++G** methodologies. In the 2PY−NH_3 and 2HP−NH_3 complexes, the ammonia molecule acts both as a proton donor and a proton acceptor. There is no known example of a single ammonia molecule acting simultaneously as a hydrogen-bond donor and acceptor in the gas phase.[14] Apparently, these complexes are the first exception to this rule. The interaction between 2PY and NH_3 has been studied in the past, and as far as we know, there are two important papers[15,16] on this subject. Held and Pratt[15] have reported the experimental gas-phase structures of 2PY−NH_3 and 2PY−$(NH_3)_2$ in their S_0 and S_1 electronic states. Theoretically, Del Bene has studied, in the gas phase with the MP2 method, only the 2PY−NH_3 complex.[16] This author has concluded that there is a discrepancy between the experimental and the computed description of the N−H···O hydrogen bond in which NH_3 acts as the proton donor. However, good agreement exists between the computed and the experimental structure in the region of the N−H···N hydrogen bond in which NH_3 is the proton-acceptor molecule. For the interaction between 2HP and NH_3, neither theoretical nor experimental data are available.

The aim of this work is

(1) to clarify the discrepancy between the experimental and the computed structures of the N−H···O interaction in 2PY−NH_3,

(2) to determine the structures of the 2HP−NH_3 and 2HP−$(NH_3)_2$ complexes and to compare these with the structures of the 2PY−NH_3 and 2PY−$(NH_3)_2$ complexes,

(3) to determine the stability difference between 2PY and 2HP complexed with one and two ammonia molecules,

(4) to compare the structural parameters and the rotational constants for the 2PY−NH_3 and 2PY−$(NH_3)_2$ complexes with corresponding experimental data as well as with MP2 results, and

(5) to study the cooperative effect in the heterotrimer systems.

Methodology

The geometries and vibrational frequencies were computed with the density functional theory using the combined Becke's three-parameter exchange functional and the gradient-corrected functional of Lee, Yang, and Parr (B3-LYP method[17,18]). This functional has been shown to predict more reliable rotational constants, geometries, and vibrational frequencies for hydrogen-bonded systems involving the DNA bases, when compared with other functionals as well as with conventional ab initio methods.[19−24] All calculations have been performed with the standard basis set 6-31++G**.

As has been noted in the past, the B3-LYP functional does not account for the dispersion forces.[25,26] It is therefore very interesting to calculate the energies also with a method taking into account this part of energy (as the MP2 method) and to compare the two sets of obtained results. For this purpose, the total energies of the different complexes were calculated at the MP2 level using the same basis set (the Möller−Plesset second-order energy was calculated with the B3-LYP/6-31++G** optimal geometry: MP2/6-31++G**//B3-LYP/6-31++G** (single point level)).

The computed total energy (E_T), with B3-LYP and MP2 methods, for each system includes the zero-point vibrational energy calculated by the DFT and MP2 methods with a scaling factor of 0.97. This scaling factor was used because the vibrational frequencies are only calculated with the DFT method.

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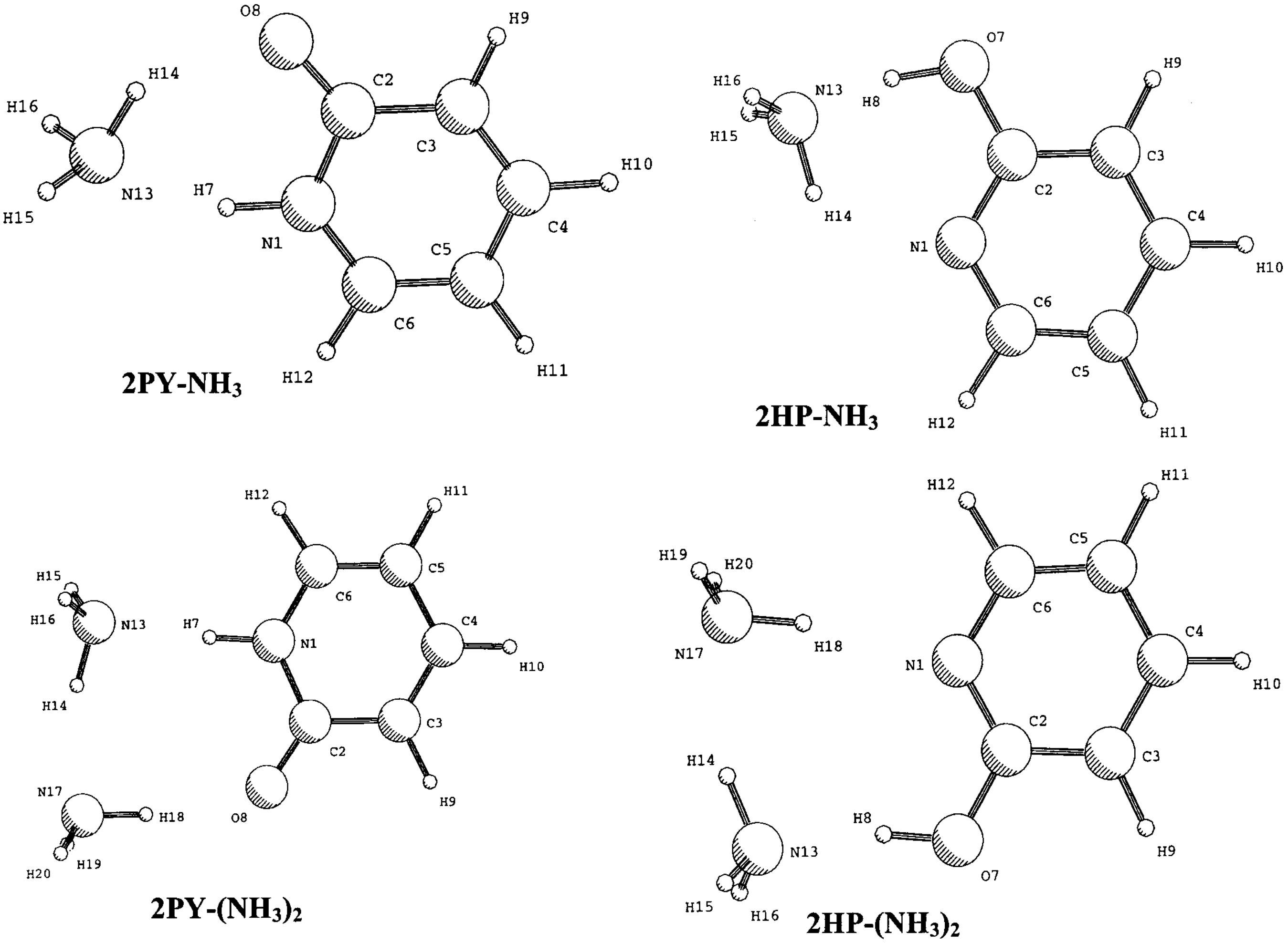
SCHEME 1: Structure of the Complexes Considered in This Work



2PY-NH$_3$ **2HP-NH$_3$** **2PY-(NH$_3$)$_2$** **2HP-(NH$_3$)$_2$**

The interaction energy was then calculated as the difference of the total energy between the complex and the separate subunits. Additionally, the Boys–Bernadi[27] counterpoise correction was applied to give the BSSE-corrected interaction energies (dissociation energy D_0).

To estimate the cooperative effect in the heterotrimers, the cooperative effect will be quantitatively measured by the additive interaction energy defined as

$$\Delta E_{\rm add} = \Delta E_{\rm X-(NH3)2} - \Delta E_{\rm X-NH3} - \Delta E_{\rm (NH3)2} \qquad X = 2PY \text{ or } 2HP \quad (1)$$

where $\Delta E_{\rm X-(NH_3)_2}$ is the interaction energy of the heterotrimers, $\Delta E_{\rm X-NH_3}$ is the interaction energy of the heterodimers, and $\Delta E_{\rm (NH_3)_2}$ is the interaction energy of the ammonia dimer.

Also, a suitable method to evaluate the H-bond cooperativity is to calculate the ratio between the frequency shift of the donor NH in the heterotrimer, $\Delta\nu'_{\rm NH}$, and in the heterodimer, $\Delta\nu_{\rm NH}$,

$$A_{\rm b} = \Delta\nu'_{\rm NH}/\Delta\nu_{\rm NH} \qquad (2)$$

The cooperative factor ($A_{\rm b}$) defined in this way is larger than 1, since it is a clear indication of the strengthening of a particular hydrogen bond by the formation of other hydrogen bonds of opposite nature, i.e., of proton-donor instead of proton-acceptor nature, within the same system.[28,29]

Finally, the IR frequencies and intensities were computed by the B3-LYP method using analytical derivative procedures implemented in the Gaussian 94 program.[30]

Results and Discussion

Structural Properties. *2PY–NH$_3$ and 2HP–NH$_3$ Complexes.* The structures of the complexes are shown in Scheme 1. Each complex is stabilized by two distorted hydrogen bonds: $N_1-H_7\cdots N_{13}$ and $N_{13}-H_{14}\cdots O_8$ for 2PY–NH$_3$ and $O_7-H_8\cdots N_{13}$ and $N_{13}-H_{14}\cdots N_1$ for 2HP–NH$_3$. In each complex, the ammonia molecule behaves as proton donor and as proton acceptor. Table 1 contains the selected structural properties calculated for these two heterodimers as well as the experimental data reported by Held and Pratt.[15]

For the 2PY–NH$_3$ complex, we discuss the results in the order of linearity of the H-bonds ($N_{13}-H_{14}\cdots O_8$ is more nonlinear than $N_1-H_7\cdots N_{13}$). The computed intermolecular distances $R(N_1-N_{13})$ and $R(N_{13}-H_7)$ are 2.91 and 1.94 Å and are in good agreement with the experimental values (2.94 and 1.99 Å, respectively). Our results show that the B3-LYP method gives results in excellent agreement with the MP2/6-31+G** data.[16] The computed angles $\angle(N_1-H_{7-13})$ and $\angle(N_{13}-N_1-C_2)$ agree well with the experimental values as well as with the MP2 calculations. Thus, in the region where NH$_3$ is a proton acceptor, there is good agreement between the theoretical and the experimental structures. For the $N_{13}-H_{14}\cdots O_8$ bond, in which NH$_3$ is a proton donor, there is a disagreement between the computed and the experimental structure. For instance, the B3-LYP $R(H_{14}-O_8)$ distance is 2.20 Å, in good agreement with the MP2 result (2.22 Å) but much shorter than the experimental distance (2.91 Å), which is an unusually long distance. The angle calculated with B3-LYP (138.4°) is very close to the MP2 value

TABLE 1: Selected Structural Data for 2-Pyridone−NH_3 and 2-Hydroxypyridine−NH_3 Complexes[a]

	B3-LYP	exp[c]
2-Pyridone−NH_3		
$N_1-H_7\cdots N_{13}$ bond		
$R(N_1-N_{13})$	2.91	2.94
$R(N_{13}-H_7)$	1.94	1.99
$r(N_1-H_7)$	1.034 (0.021)[b]	
$\angle(N_1-H_7-N_{13})$	155.1	154.2
$\angle(N_{13}-N_1-C_2)$	98.5	96.9
$O_8\cdots H_{14}-N_{13}$ bond		
$R(N_{13}-O_8)$	3.04	
$R(H_{14}-O_8)$	2.20	2.91
$r(N_{13}-H_{14})$	1.024 (0.008)	
$r(N_{13}-H_{15})$	1.017 (0.001)	
$r(C_2{=}O_8)$	1.242 (0.010)	
$\angle(H_{15}-N_{13}-H_{16})$	107.5 (−0.6)	
$\angle(N_{13}-H_{14}-O_8)$	138.4	87.2
$\angle(N_{13}-O_8-C_2)$	96.5	
2-Hydroxypyridine−NH_3		
$O_7-H_8\cdots N_{13}$ bond		
$R(O_7-N_{13})$	2.75	
$R(H_8-N_{13})$	1.755	
$r(O_7-H_8)$	1.003 (0.032)	
$r(C_2-O_7)$	1.340 (−0.017)	
$\angle(O_7-H_8-N_{13})$	171.5	
$N_1\cdots H_{14}-N_{13}$ bond		
$R(N_1-N_{13})$	3.09	
$R(N_1-H_{14})$	2.43	
$r(N_{13}-H_{14})$	1.020 (0.004)	
$r(N_{13}-H_{15})$	1.016 (0.000)	
$r(N_1-C_2)$	1.340 (0.010)	
$\angle(H_{15}-N_{13}-H_{16})$	108.1 (0.00)	
$\angle(N_1-H_{14}-N_{13})$	153.4	
$\angle(N_{13}-N_1-C_2)$	89.6	

[a] Distances are in ångstrom and angles in degrees. [b] The elongation of the bond length upon complexation. [c] Reference 15.

TABLE 2: Theoretical and Experimental Rotational Constants (MHz) of 2PY/2HP−NH_3 and 2PY/2HP−$(NH_3)_2$ Complexes

	B3-LYP	exp[a]
2-Pyridone−NH_3		
A	3703	3725
B	1388	1381
C	1015	1013
mean deviation	10	
2-Hydroxypyridine−NH_3		
A	4195	
B	1302	
C	999	
2-Pyridone−$(NH_3)_2$		
A	2453	2436
B	843	840
C	632	630
mean deviation	7	
2-Hydroxypyridine−$(NH_3)_2$		
A	2264	
B	904	
C	651	

[a] Reference 15.

(137°) but much larger than the experimental value (87.2°). As our results agree well with those obtained by Del Bene,[16] a possible origin of the discrepancy between the computed and experimental descriptions of the $N_{13}-H_{14}\cdots O_8$ H-bond may be the assumption of Held and Pratt[15] that the experimental structures of 2PY and NH_3 are unchanged in the 2PY−NH_3 complex. The increase in the N−H bond length and the decrease in the ∠(H−N−H) angle of NH_3 may be responsible for the differences between the experimental and theoretical description of this bond. Because of changes in the intramolecular NH_3 coordinates upon complexation, there is no local C_3 axis of NH_3 in the computed structure. At the contrary, Held and Pratt[15] have concluded that the orientation of the local C_3 axis of NH_3 is parallel (within 10°) to the inertial axis of the complex.

The intermolecular distances $R(N_1-N_{13})$ and $R(N_{13}-O_8)$ for the 2PY−NH_3 complex are longer than the corresponding values for 2PY−H_2O.[31] This suggests that the $N-H\cdots N$ and $N-H\cdots O$ hydrogen bonds are weaker than the corresponding $N-H\cdots O$ and $O-H\cdots O$ hydrogen bonds. Changes in intramolecular coordinates in the 2PY−NH_3 are smaller than those of the corresponding intramolecular coordinates in the 2PY−H_2O system except for the N−H bond length and the non-hydrogen-bonded NH and OH bonds of NH_3 and H_2O.

For the 2HP−NH_3 complex, neither MP2 nor experimental data are available and a direct comparison with our results is not possible. However, the comparison of the structures of 2HP−NH_3 and 2PY−NH_3 show that the bonds of 2PY−NH_3 are much more nonlinear than those of 2HP−NH_3. For instance, the angles $\angle(N_1-H_7-N_{13})$ and $\angle(N_{13}-H_{14}-O_8)$ are much larger than the angles $\angle(O_7-H_8-N_{13})$ and $\angle(N_1-H_{14}-N_{13})$ of 2HP−NH_3 and smaller than 180° (which corresponds to a perfectly linear hydrogen bond). Also, the elongation of the bond length $N_{13}-H_{14}$ in 2PY−NH_3 is larger than that in 2HP−NH_3. The bond length CO increases in 2PY−NH_3, while this length decreases in 2HP−NH_3. In each complex, the ammonia molecule is a strong proton acceptor and a much weaker proton donor.

Table 2 collects the calculated rotational constants and experimental data if available. The agreement between DFT rotational constants and experimental data for 2PY−NH_3 is excellent. Note that our results predict rotational constants better than the MP2 calculation, especially for the constant A. A similar finding was reported before by Llamas-Saiz et al.[32] The overall good quality of the hybrid density functional (B3-LYP) is confirmed by this comparison. We believe that the rotational constants predicted by the DFT calculations for the 2HP−NH_3 complex, for which experimental data are not available, would be in similar agreement with the experimental data as for 2PY−NH_3.

2PY−$(NH_3)_2$ and 2HP−$(NH_3)_2$ Complexes. The selected structural data for 2PY−$(NH_3)_2$ and 2HP−$(NH_3)_2$ are listed in Table 3. We investigated in this work only the most stable structures, which are observed experimentally. These structures are similar to the most stable structure of tropolone−$(H_2O)_2$ complexes.[33] These complexes are stabilized by three nonlinear hydrogen bonds and the ammonia dimer acts both as proton donor to 2-pyridone through $N_{17}-H_{18}$ (proton acceptor from 2-hydroxypyridine at N_{17}) and as proton acceptor from 2-pyridone at N_{13} (proton donor to 2-hydroxypyridine through $N_{17}-H_{18}$). The calculations show that the most nonlinear hydrogen bond formed in the bonded ammonia dimer is the $N_{13}-H_{14}\cdots N_{17}$ bond for 2PY−$(NH_3)_2$ and 2HP−$(NH_3)_2$.

The computed intermolecular distance $R(O_8-N_{17})$ is 3.02 Å, which is in very good agreement with the experimental value (3.03 Å). The calculated intermolecular distances $R(N_{13}-N_{17})$ and $R(N_1-N_{13})$ are 0.017 Å larger and smaller, respectively, than the corresponding experimental distances. However, the calculated rotational constants are in good agreement with the experimental results. For instance, the mean deviation for the rotational constants for 2PY−$(NH_3)_2$ is only 7 MHz.

The most remarkable change in the structures of the subunits in 2PY−$(NH_3)_2$ and 2HP−$(NH_3)_2$ is the decreased intermolecular distance $R(N_{13}-N_{17})$ by about 0.2 Å compared to the

TABLE 3: Selected Structural Data for 2-Pyridone−$(NH_3)_2$ and 2-Hydroxypyridine−$(NH_3)_2$ Complexes[a]

	B3-LYP	exp[c]
2-Pyridone−$(NH_3)_2$		
$O_8 \cdots H_{18}-N_{17}$ bond		
$R(O_8-N_{17})$	3.02	3.03
$r(N_{17}-H_{18})$	1.025 (0.009)[b]	
$\angle(O_8-H_{18}-N_{17})$	168.4	
$N_{13}-H_{14} \cdots N_{17}$ bond	3.04	2.87
$R(N_{13}-N_{17})$	1.032 (0.016)	
$r(N_{13}-H_{14})$	162.0	
$\angle(N_{13}-H_{14}-N_{17})$		
$N_1-H_7 \cdots N_{13}$ bond		
$R(N_1-N_{13})$	2.92	3.09
$r(N_1-H_7)$	1.043 (0.030)	
$\angle(N_1-H_7 \cdots N_{13})$	175.7	
2-Hydroxypyridine−$(NH_3)_2$		
$O_7-H_8 \cdots N_{13}$ bond		
$R(O_7-N_{13})$	2.71	
$r(O_7-H_8)$	1.015 (0.044)	
$\angle(O_7-H_8-N_{13})$	169.2	
$N_{13}-H_{14} \cdots N_{17}$ bond		
$R(N_{13}-N_{17})$	3.03	
$r(N_{13}-H_{14})$	1.029 (0.013)	
$\angle(N_{13}-H_{14}-N_{17})$	158.3	
$N_{17}-H_{18} \cdots N_1$ bond		
$R(N_1-N_{17})$	3.17	
$r(N_{17}-H_{18})$	1.026 (0.01)	
$\angle(N_{17}-H_{18}-N_1)$	173.3	

[a] Distances are in ångstrom and angles in degrees. [b] The elongation of the bond length upon complexation. [c] Reference 15.

ammonia dimer. This decrease is due to the formation of stronger hydrogen bonds to 2PY and 2HP, respectively, and this reflects both the cooperativity effect and the distortion in these systems. Also, the hydrogen-bonded $N_{13}-H_{14}$ and $N_{17}-H_{18}$ bond lengths in the two ammonia molecules increase by 0.016 and 0.009 Å for 2PY−$(NH_3)_2$, and by 0.013 and 0.010 Å for 2HP−$(NH_3)_2$. A larger increase of N_1-H_7 of 2-pyridone and of O_7-H_8 of 2-hydroxypyridine is also noted. The increases in the hydrogen-bond strengths are related to the cooperativity effect in the following scheme: $N_1-H_7 \cdots N_{13}-H_{14} \cdots N_{17}-H_{18} \cdots O_8$ for 2PY−$(NH_3)_2$ and $N_1 \cdots H_{18}-N_{17} \cdots H_{14}-N_{13} \cdots H_8-O_8$ for 2HP−$(NH_3)_2$.

Energetics and Dipole Moments. The energies, the interaction energies (D_e), the binding energies (D_0), the additive interaction energies (ΔE_{add}), and the dipole moments of the complexes are listed in Table 4.

The relative energy, ΔE, between 2PY−NH_3 and 2HP−NH_3 is 0.93 kJ/mol, calculated with B3-LYP, in favor of the oxo form and 7.4 kJ/mol calculated with MP2 in favor of the hydroxy form. This difference originates from the discrepancy of the energies of the monomers calculated by DFT and MP2 (DFT predicts that 2PY is more stable than 2HP by 1.5 kJ/mol, while MP2 predicts a relative energy of 9.3 kJ/mol in favor of the hydroxy form). The same effect can be noted for the 2PY−$(NH_3)_2$ and 2HP−$(NH_3)_2$ complexes. We mention that similar discrepancies between ΔE computed with conventional methods and DFT have been found for 2PY/2HP−H_2O complexes[31] and for thio- and selenocytosine.[34]

The interaction energy (D_e) is −43.3 kJ/mol for 2PY−NH_3. This result indicates that 2PY−NH_3 is about 6 kJ/mol less stable than the corresponding 2PY−H_2O complex, which has previously been noted from the comparison of changes of the coordinates of the monomers. Note that the MP2 calculations predict similar results. For the 2HP−NH_3 complex, the interaction energy is −43.5 kJ/mol, which is similar to the value of 2HP−H_2O (D_e = −43.7 kJ/mol). The interaction energies obtained for both complexes show a slight hydrogen-bond fortification due to the cooperativity between the two H-bonds in the complex. A similar conclusion has been noted in the former studies.[31,35] The correction for ZPE and BSSE decreases the interaction energy of the 2PY−NH_3 complex to −31.4 kJ/mol (DFT) and −31.0 kJ/mol (MP2), and for 2HP−NH_3 to −30.4 kJ/mol (DFT) and −27.0 kJ/mol (MP2). Both DFT and MP2 methods indicate that 2PY interacts slightly more strongly with a single ammonia molecule than 2HP. For instance, B3-LYP predicts that 2PY−NH_3 is more stable than 2HP−NH_3 by 1 kJ/mol, while MP2 predicts 4 kJ/mol of difference.

The dissociation energy (D_0) of 2PY−$(NH_3)_2$ is −49.6 kJ/mol (DFT) and −48.7 kJ/mol (MP2) relative to 2-pyridone and the ammonia dimer, while the dissociation energy of the 2HP−$(NH_3)_2$ complex is −46.2 kJ/mol (DFT) and −44.3 kJ/mol relative to 2-hydroxypyridine and the ammonia dimer. Thus, 2PY interacts more strongly with two ammonia molecules by 3.4 or 4.4 kJ/mol than 2HP.

We also note that the additive interaction energy defined in eq 1 is −6.3 kJ/mol (DFT) and −7.0 kJ/mol (MP2) for 2PY−$(NH_3)_2$, while this energy is −0.9 kJ/mol (DFT) and −1.1 kJ/mol (MP2) for 2HP−$(NH_3)_2$. The cooperative effects are nearly 7 times larger for 2PY−$(NH_3)_2$ than for 2HY−$(NH_3)_2$, because the values of D_e differ about 6 kJ/mol (DFT) and 8 kJ/mol (MP2). These results reflect the cooperative effect in the following scheme: $N_1-H_7 \cdots N_{13}-H_{14} \cdots N_{17}-H_{18} \cdots O_8$ and $N_1 \cdots H_{18}-N_{17} \cdots H_{14}-N_{13} \cdots H_8-O_7$.

For each complex, the interaction energy corrected with ZPE and BSSE computed with B3-LYP is close to the value calculated with MP2. This comparison is very interesting, because the MP2 method is generally considered as the standard method for studying intermolecular interactions such as hydrogen bonding.

Vibrational Analysis. The selected intramolecular frequencies ν_{NH}, ν_{OH}, and ν_{CO} for 2PY/2HP−NH_3 and 2PY/2HP−$(NH_3)_2$ complexes are presented in Table 5. Theses modes are studied because they are not only very intense, which allows their observation by matrix-isolation or supersonic jet, as has been demonstrated for 2PY−H_2O,[31,36] but they are also strongly perturbed upon formation of a hydrogen bond. Therefore, they

TABLE 4: Energies (au), Relative Energies (kJ/mol), Interaction Energies (D_e, in kJ/mol), Dissociation Energgies (D_0, in kJ/mol), Dipole Moments (D), and Additive Interaction Energies (ΔE, in kJ/mol) for 2PY/2HP−$(NH_3)_n$ (n = 1, 2)

	2PY−NH_3		2HP−NH_3		2PY−$(NH_3)_2$		2HP−$(NH_3)_2$	
	B3-LYP	MP2	B3-LYP	MP2	B3-LYP	MP2	B3-LYP	MP2
E	−380.1281089	−379.0036098	−380.1274681	−379.0061261	−436.7090293	−435.4114161	−436.7061697	−435.4116742
ZPE	0.1272106	0.1272106	0.1269245	0.1269245	0.1636070	0.1636070	0.1632316	0.1632316
E_T	−380.0008983	−378.8763992	−380.0005436	−378.8792016	−436.5454223	−435.2478091	−436.5429381	−435.2484426
ΔE	0.00	7.4	0.93	0.00	0.00	1.7	6.5	0.0
D_e	−43.3	−50.3	−43.5	−48.0	−64.6	−73.8	−58.9	−65.6
D_0	−31.4	−31.0	−30.4	−27.0	−49.6	−48.7	−46.2	−44.3
ΔE_{add}	-				−6.3	−7.0	−0.9	−1.1
μ	3.21	3.58	1.93	2.02	2.92	3.29	1.80	1.91

TABLE 5: Selected Vibrational Data for 2PY/2HP−NH_3 and 2PY/2HP−$(NH_3)_2$ Complexes Calculated with DFT/B3-LYP/6-31++G**

	frequency (cm^{-1})	frequency shift (cm^{-1})[a]	intensity (km/mol)
	2-Pyridone−NH_3		
ν_{NH}	3223	−382	788
$\nu_{NH}{}^{b}$	3421	−159	112
ν_{CO}	1740	−13	627
	2-Hydroxypyridine−NH_3		
ν_{OH}	3111	−658	1718
$\nu_{NH}{}^{b}$	3457	−123	49
ν_{CO}	1351	21	92
	2-Pyridone−$(NH_3)_2$		
ν_{OH}	3071	−534	1419
$\nu_{N13H14}{}^{b}$	3282	−298	371
$\nu_{N17H18}{}^{b}$	3400	−180	351
ν_{CO}	1728	−25	608
	2-Hydroxypyridine−$(NH_3)_2$		
ν_{OH}	2898	−871	2362
$\nu_{N13H14}{}^{b}$	3326	−254	289
$\nu_{N17H18}{}^{b}$	3384	−196	332
ν_{CO}	1364	34	65

[a] The shifts are with respect to the subunit monomers; for the NH_3 monomer, the frequency ν_{NH} is the average of the three stretching frequencies.

represent the ideal spectroscopy to study the hydrogen-bonded complexes. The shifts are computed with respect to the monomer harmonic frequencies ($\nu_{NH} = 3605$ cm^{-1}, $\nu_{CO} = 1753$ cm^{-1} for 2PY; $\nu_{OH} = 3769$ cm^{-1}, $\nu_{CO} = 1330$ cm^{-1} for 2HP) and to the average of the NH stretching frequencies in NH_3 (3580 cm^{-1}). The frequency shifts of the NH and OH modes for the heterodimers are very large, as previously predicted from the changes of the coordinates Δr(NH) and Δr(OH), the red shifts being −382 and −658 cm^{-1}, respectively. Also, the shift $\Delta\nu$(OH) is much larger than the shift $\Delta\nu$(NH). One explanation for this difference is the strong nonlinearity of the $N_1{-}H_7{\cdots}N_{13}$ bond compared to the $O_7{-}H_8{\cdots}N_{13}$ bond, as was indicated in Table 1. As will be demonstrated in our future work,[37] the hydrogen-bond angle distortion reduces the local hydrogen-bond strength. The two NH stretching frequencies of ammonia in the 2PY−NH_3 and 2HP−NH_3 complexes are 3421 and 3457 cm^{-1}, respectively. The red shift of the NH mode in 2PY−NH_3 is slightly larger than the value for 2HP−NH_3, which reflects the stronger H-bond in 2PY−NH_3. The calculated frequency of the ν_{CO} mode in 2PY−NH_3 is 1740 cm^{-1}. The value scaled with a scaling factor of 0.975 is very close to the experimental value in the 2PY−H_2O complex.[31,36] Contrary to the red shift of the ν_{CO} mode in 2PY−NH_3, the shift $\Delta\nu_{CO}$ in the 2HP−NH_3 complex is blue, which is consistent with our previous result for the elongation of the bond length r(CO). In the heterotrimer complexes, we note an increased frequency shift of the three modes ν_{NH}, ν_{OH}, and ν_{CO} compared to the heterodimers, and these results reflect the cooperative effect existing in the three H-bonds in the heterotrimers. The calculated cooperativity factors A_b are 1.9 and 2.1 for 2PY−$(NH_3)_2$ and 2HP−$(NH_3)_2$, respectively. These values are similar to the results recently obtained by Gonzalez et al.[38] for the ethanol trimers.

Conclusions

Several important points emerge from this study:

1. The complexes 2PY−NH_3 and 2HP−NH_3 are stabilized by two distorted hydrogen bonds N−H···N−H···O and O−H···N−H···N, respectively, while the heterotrimers are stabilized by three nonlinear hydrogen bonds N−H···N−H···N−H···O and O−H···N−H···N−H···N, respectively.

2. The computed rotational constants of 2PY−NH_3 and 2PY−$(NH_3)_2$ agree well with the experimental results. The computed structures of these complexes are in agreement with the experimental structures except for the description of the N−H···O hydrogen bond, where NH_3 is the proton donor. Our calculations for the 2PY−NH_3 complex agree very well with those obtained with the MP2 method.

3. In the gas phase, 2PY interacts more strongly than 2HP with a single as well as with a dimer ammonia molecule.

4. In the 2PY−$(NH_3)_2$ and 2HP−$(NH_3)_2$ complexes, the cooperative effects are very large, as noted by the intermolecular distance $R(N_{13}{-}N_{17})$, the elongation of the NH bond length, the frequency shift of the ν(NH) mode (measured A_b), and the additive interaction energy.

5. The dissociation energies (D_0) computed with B3-LYP//B3-LYP/6-31++G** and MP2//B3-LYP/6-31++G** are similar. This indicates that the density functional theory is very promising for the study of the intermolecular interaction in this range of energy.

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