

NMR and *Ab initio* Studies of Small Complexes Formed between Water and Pyridine Derivatives in Solid and Liquid Phase

Shasad Sharif,[†] Ilja G. Shenderovich,^{†‡*} Leticia González,[†] Gleb S. Denisov,[‡] David N. Silverman[§]
and Hans-Heinrich Limbach^{†*}

Supporting Materials

Table of Contents

Figure S1.	¹ H NMR spectra of a mixture of ¹⁵ N labeled pyridine : H ₂ O in freon mixture.	S2
Figure S2.	The ¹⁵ N spectra of heterocyclic water mixtures at different temperatures.	S3
Figure S3.	MP2 optimized structures of the pyridine-water clusters.	S4
Figure S4.	Plot of pK _a against the ¹⁵ N chemical shift $\delta(\text{OH}\underline{\text{N}})$.	S5
Table S1.	$\rho_{\text{HN}}(r)$, $\nabla^2\rho(r)$ and $H(r)$ at the corresponding bond critical points.	S6
Table S2.	NMR parameters of pyridine-water clusters at DFT and MP2 level of theory.	S7
Table S3.	NMR parameters of pyridine-water clusters at DFT and MP2 level of theory.	S8

* To whom correspondence should be addressed. E-mail: limbach@chemie.fu-berlin.de (H.-H. Limbach); shender@chemie.fu-berlin.de (I. G. Shenderovich)

[†] Institut für Chemie und Biochemie, Freie Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany

[‡] Institute of Physics, St. Petersburg State University, 198504 St. Petersburg, Russian Federation

[§] Box 100267 Health Center, University of Florida, FL 32610-0267 Gainesville, USA

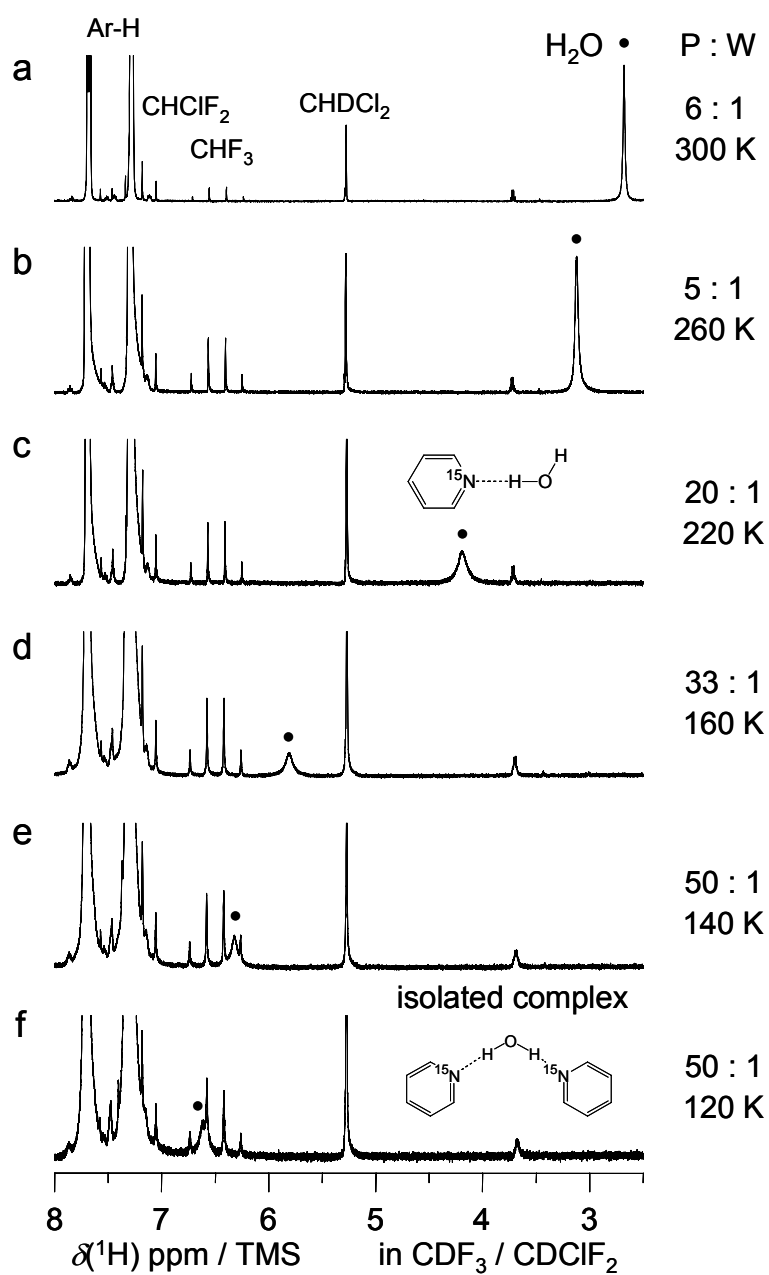


Figure S1. ^1H NMR liquid state spectra of ^{15}N -pyridine-water complex in freon mixture $\text{CDF}_3/\text{CDCIF}_2$. The water signal (filled circle) appears at (a) 2.7 ppm, (b) 3.1 ppm, (c) 4.2 ppm, (d) 5.8 ppm, (e) 6.3 ppm, (f) 6.6 ppm.

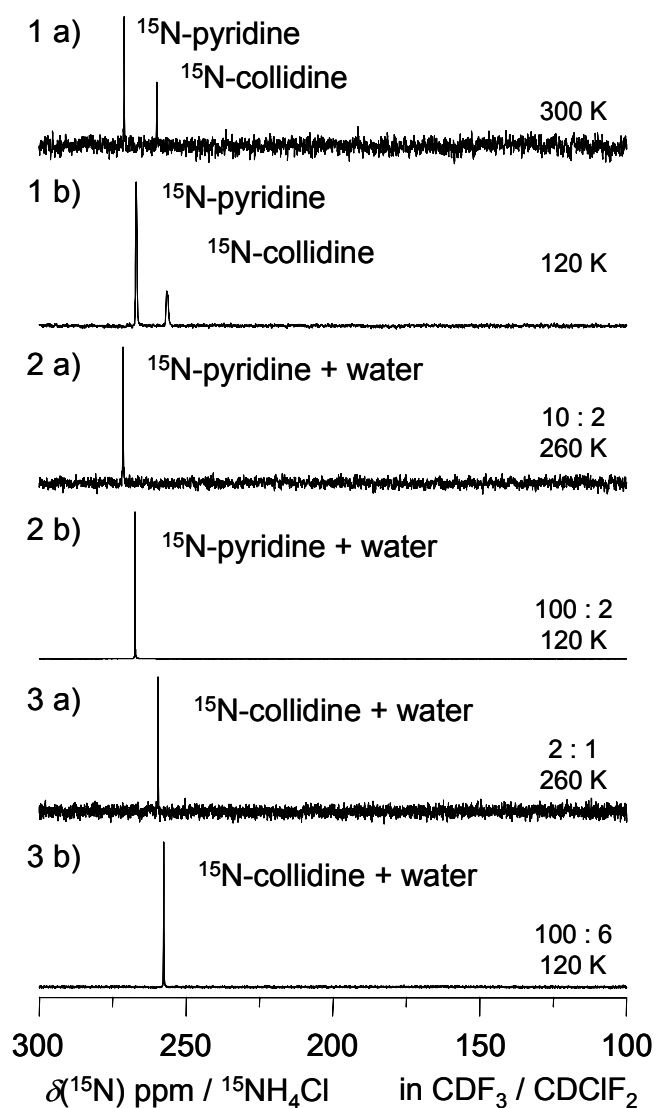


Figure S2. ^{15}N $\{^1\text{H}\}$ NMR spectra of ^{15}N labeled collidine and pyridine in the freonic mixture. All spectra are referenced to the external solid $^{15}\text{NH}_4\text{Cl}$. 1) collidine and pyridine a) 271.1 and 260 ppm, b) 267.0 and 256.5 ppm. 2) mixture of water and pyridine a) 271.4, and b) 267.4 ppm. 3) mixture of water and collidine a) 259.6, and b) 257.6 ppm.

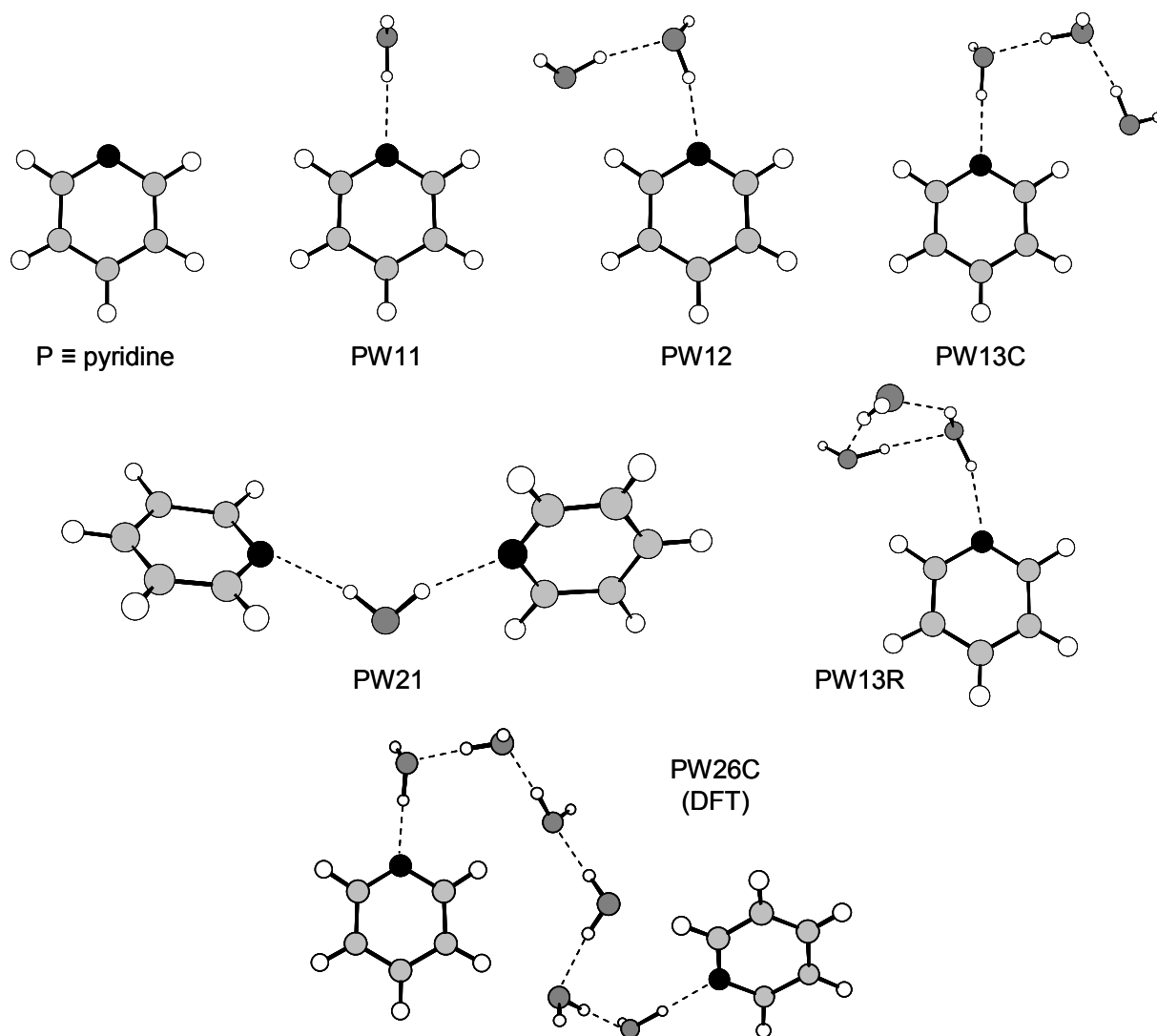


Figure S3. MP2/6-31+G(d) optimized structures of the pyridine(P)-water (W) clusters investigated in this study. The numbers included on the label denote the proportion pyridine : water; additionally, C stands for chain and R for ring. The DFT structures are qualitatively similar and therefore not shown, except for the PW26C cluster.

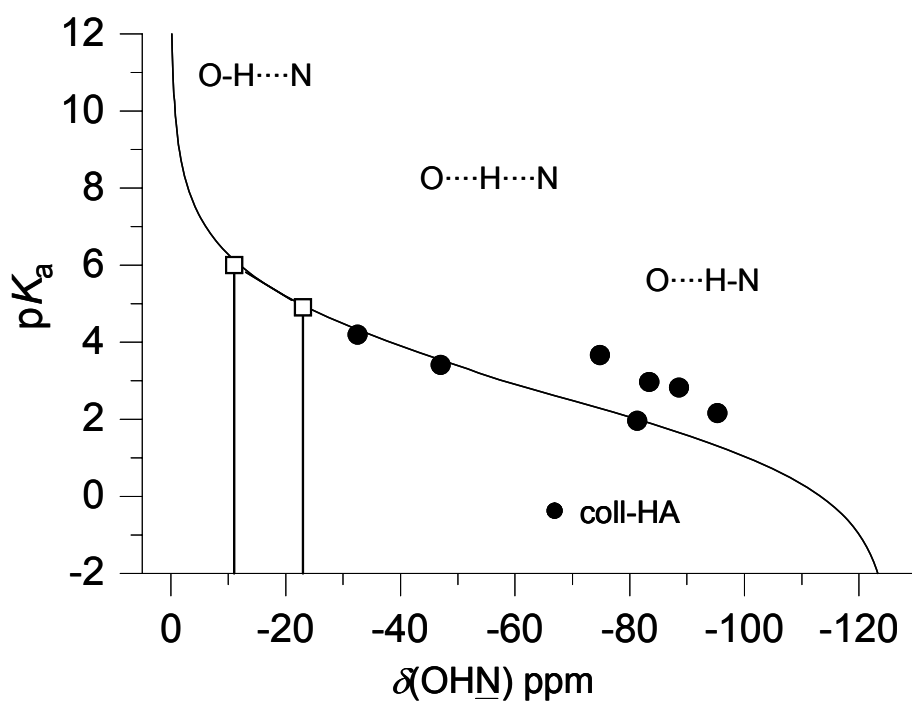


Figure S4. Plot of $\text{p}K_a$ against the ^{15}N chemical shift $\delta(\text{OHN})$ of collidine-carboxylic acid complexes in the organic solid state. The filled circles refer to the collidine-HA complexes obtained from previous work (see main text) in organic solid state. (\square) represent the expected $\text{p}K_a$ values of 6.0 for the symmetric species at -11 ppm and 4.9 for the asymmetric species at -23 ppm of the collidine-water mixtures in the frozen phase. For the calculation of the correlation curves see main text.

TABLE S1: Charge density $\rho_{\text{HN}}(\mathbf{r})$ and its Laplacian $\nabla^2\rho(\mathbf{r})$ as well as the energy density $H(\mathbf{r})$ at the corresponding bond critical points of the pyridine and collidine-(H₂O)_n clusters with $n = 0.5, 1, 2, 3, 6$ at DFT level of theory.

pyridine	n	r_{NH} / Å	$\rho_{\text{HN}}(\mathbf{r})$ a. u.	$\nabla^2\rho(\mathbf{r})$ a. u.	$H(\mathbf{r})$ a. u.
B3LYP/6-311++G(2df,2p)//B3LYP/6-31+G(d,p)					
PW21 ^{a)}	½	2.022 (2.018)	0.0250 (0.0247)	0.0717 0.0693	-0.00035 -0.00008
PW11	1	1.932	0.0309	0.0795	0.00125
PW12	2	1.830	0.0394	0.0862	0.00466
PW13C	3	1.783	0.0440	0.0792	0.00808
PW13R	3	1.883	0.0347	0.0827	0.00282
B3LYP/6-311++G(2df,2p)//B3LYP/6-31+G(d,p)					
CW21 ^{a)}	½	2.021 (2.019)	0.0256 (0.0258)	0.0684 0.0706	0.00009 -0.00018
CW11	1	1.915	0.0326	0.0025	0.07575
CW12	2	1.837	0.0389	0.0781	0.00537
CW13C	3	1.784	0.0429	0.0845	0.00642
CW13R	3	1.874	0.0358	0.0771	0.00396

^a Values in parenthesis correspond to the second OHN hydrogen bond.

TABLE S2: NMR parameters of pyridine-(H₂O)_n clusters with n = 0.5, 1, 2, 3, 6 at DFT and MP2 levels of theory.

pyridine	n	σ^a / ppm	σ_{XX}^a / ppm	σ_{YY}^a / ppm	σ_{ZZ}^a / ppm	$\delta(^{15}\text{N})^b$ / ppm	$\delta(^{15}\text{N})^c$ / ppm	$\delta(^{15}\text{N})^d$ / ppm
B3LYP/6-311++G(2df,2p)//B3LYP/6-31+G(d,p)								
P	0	-105.37	-254.35	-348.26	286.50	0	306.65	338.40
PW21 ^{d)}	½	-93.12 (-93.04)	-161.14 (-163.89)	-69.38 (-102.12)	-48.84 (-13.12)	-12.25 (-12.32)	294.40 (294.32)	326.15 (326.07)
PW11	1	-86.92	-181.53	-356.78	277.54	-18.44	288.20	319.95
PW12	2	-79.91	-216.03	-296.96	273.25	-25.46	281.19	312.94
PW13C	3	-76.24	-213.07	-284.15	268.50	-29.13	277.52	309.27
PW13R	3	-83.95	-201.68	-307.85	257.67	-21.41	285.23	316.98
PW26C	6	-72.33	-300.81	-174.30	258.11	-33.03	273.61	305.36
	6	-75.52	-243.95	-160.29	177.67	-29.84	276.80	308.55
MP2/6-311++G(d,p)//MP2/6-31+G(d)								
P	0	-110.82	-269.97	-362.70	300.21	0	314.17	351.58
PW21 ^{d)}	½	-96.29 (-96.24)	-183.88 (-183.42)	-32.49 (-31.78)	-72.51 (-73.52)	-14.52 (-14.58)	299.65 (299.60)	337.05 (337.00)
PW11	1	-89.68	-195.35	-367.93	294.22	-21.14	293.04	330.44
PW12	2	-82.34	-230.46	-308.25	291.69	-28.48	285.69	323.10
PW13C	3	-78.56	-224.91	-296.12	285.36	-32.26	281.91	319.32
PW13R	3	-87.77	-219.48	-318.42	274.59	-23.05	291.13	328.53

^a Over GIAO calculated chemical shifts σ as well as the diagonal elements of the tensor σ_{XX} , σ_{YY} , σ_{ZZ} .

^b ¹⁵N chemical shifts are given with respect to free pyridine calculated at the same level of theory, with shielding of the free heterocyclic nitrogen atom of -105.37 (DFT) and -110.82 ppm (MP2). ¹⁵N chemical shift are referenced to external solid ¹⁵NH₄Cl. ^c from ammonia NH_{3(g)}, shielding is 258.56 (DFT) and 260.64 ppm (MP2), by recalculation it to solid ¹⁵NH₄Cl with -57.28 ppm. ^d from ammonium NH₄⁺, shielding is 233.03 (DFT) and 240.76 ppm (MP2). ^e Values in parenthesis correspond to the second OHN hydrogen bond.

TABLE S3: NMR parameters of collidine-(H₂O)_n clusters with n = 0.5, 1, 2, 3 at DFT and MP2 levels of theory.

collidine	n	σ^a / ppm	σ_{XX}^a / ppm	σ_{YY}^a / ppm	σ_{ZZ}^a / ppm	$\delta(^{15}\text{N})^b$ / ppm	$\delta(^{15}\text{N})^c$ / ppm	$\delta(^{15}\text{N})^d$ / ppm
B3LYP/6-311++G(2df,2p)//B3LYP/6-31+G(d,p)								
C	0	-91.54	-166.49	-365.05	256.91	0	292.82	324.57
CW21 ^{e)}	½	-79.11 (-78.80)	-144.84 (-144.46)	-212.08 (-210.03)	119.59 (118.09)	-12.42 (-12.74)	280.39 (280.07)	312.14 (311.83)
CW11	1	-72.71	-155.83	-309.18	246.89	-18.84	273.98	305.73
CW12	2	-66.32	-142.54	-271.37	214.94	-25.22	267.60	299.35
CW13C	3	-62.43	-118.14	-231.91	162.76	-29.11	263.71	295.46
CW13R	3	-69.63	-162.65	-290.41	244.17	-21.91	270.91	302.66
CW26C ^{e)}	6	-62.30 -60.59	-52.97 -158.37	-248.13 -81.79	114.19 58.39	-29.24 -30.95	263.58 261.87	295.33 293.62
MP2/6-311++G(d,p)//MP2/6-31+G(d)								
C	0	-87.31	-175.13	-354.95	268.15	0	290.66	328.07
CW21 ^{e)}	½	-77.19 (-77.32)	-112.89 (-113.73)	-201.52 (-200.67)	82.83 (82.43)	-10.12 (-9.98)	280.55 (280.68)	317.95 (318.08)
CW11	1	-66.49	-160.75	-302.48	263.77	-20.82	269.84	307.25
CW12	2	-59.80	-137.35	-264.97	222.92	-27.51	263.16	300.56
CW13C	3	-57.48	-190.92	-239.69	258.17	-29.83	260.83	298.24
CW13R	3	-63.13	-177.67	-276.46	264.75	-24.18	266.48	303.89

^a Over GIAO calculated chemical shifts σ as well as the diagonal elements of the tensor σ_{XX} , σ_{YY} , σ_{ZZ} .

^b ¹⁵N chemical shifts are given with respect to free collidine calculated at the same level of theory, with shielding of the free heterocyclic nitrogen atom of -91.54 (DFT) and -87.31 ppm (MP2). ¹⁵N chemical shift are referenced to external solid ¹⁵NH₄Cl. ^c from ammonia NH_{3(g)}, shielding is 258.56 (DFT) and 260.64 ppm (MP2), by recalculation it to solid ¹⁵NH₄Cl with -57.28 ppm. ^d from ammonium NH₄⁺, shielding is 233.03 (DFT) and 240.76 ppm (MP2). ^e Values in parenthesis correspond to the second OHN hydrogen bond.