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Characterizing the $n \rightarrow \pi^*$ interaction of pyridine with small ketones: a rotational study of pyridine···acetone and pyridine···2-butanone

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Supporting Information

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Gaussian 16, Revision A.03,

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Figure S1. The rotational spectrum of a mixture of pyridine (PY) and 2-butanone (2BU) where the rotational transitions of the complex PY···2BU have been identified.

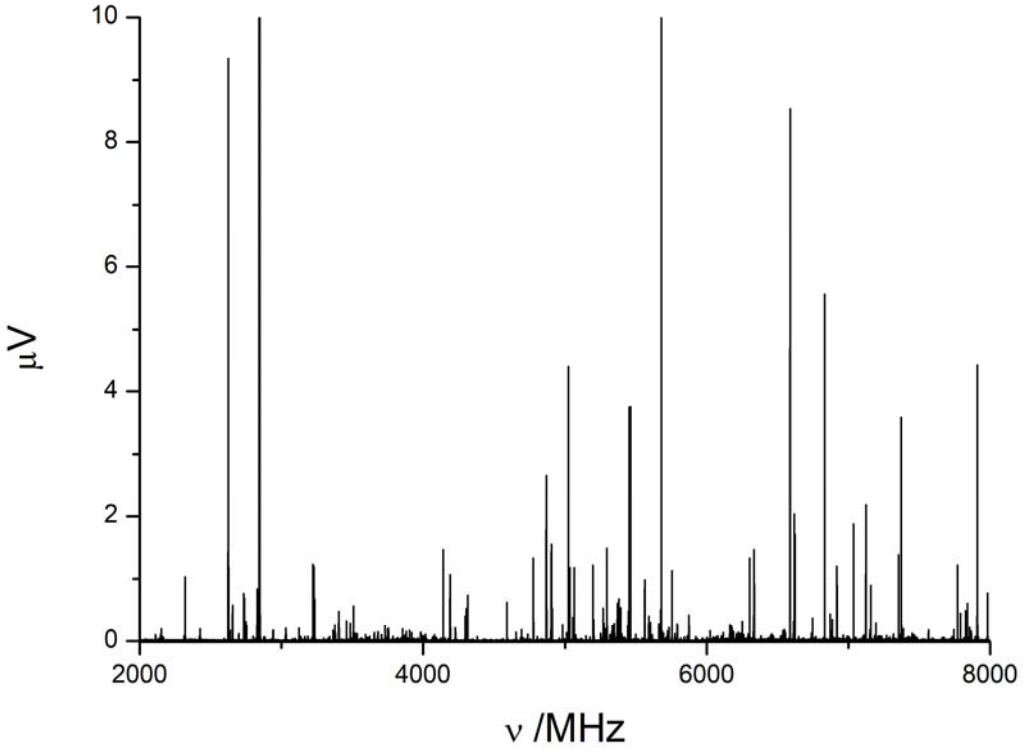


Figure S2. The rotational spectrum of a mixture of pyridine (PY) and acetone (ACE) where the rotational transitions of the complex PY···ACE have been identified.

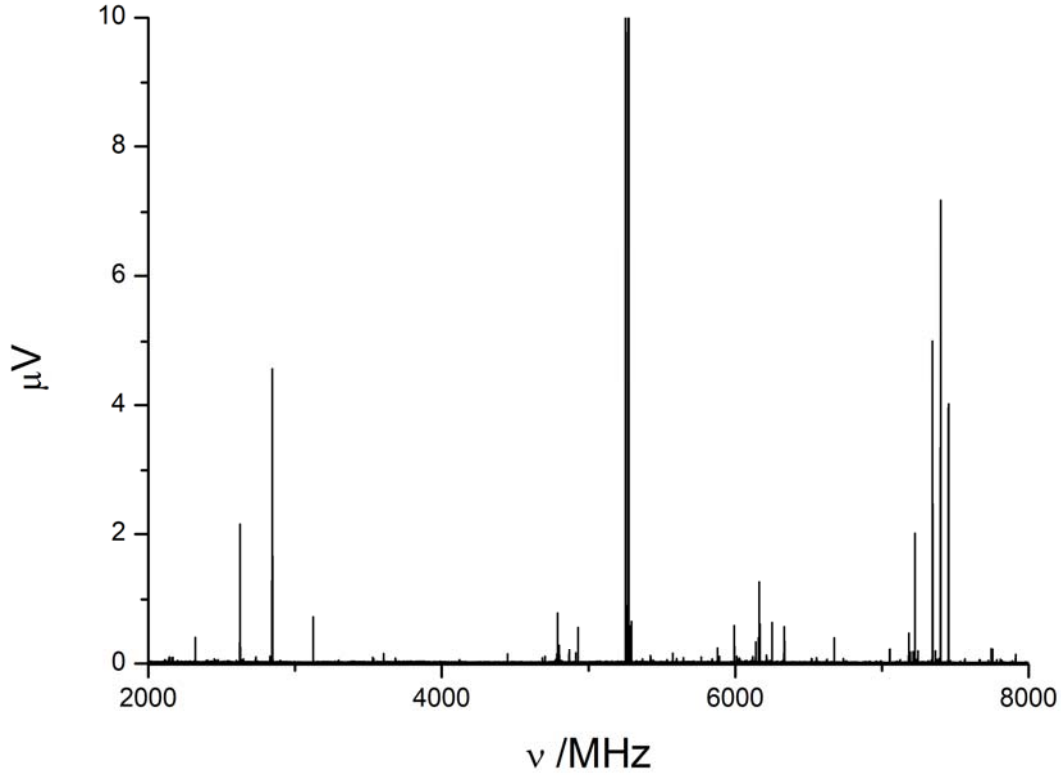
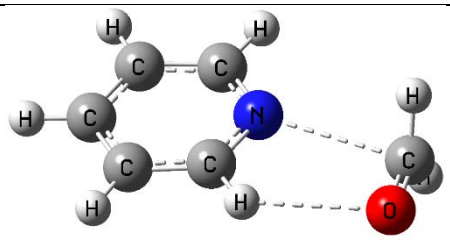
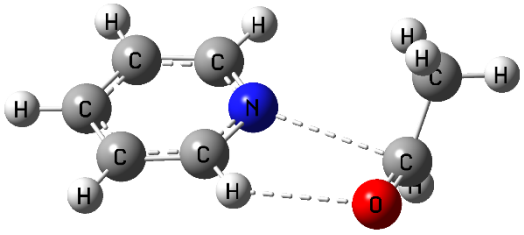


Figure S3. The most stable configuration for the pyridine···acetone and pyridine···2-butanone complexes corresponds to the one presenting a $n \rightarrow \pi^*$ tetrel bond. For comparative purposes, the geometries of pyridine···formaldehyde and pyridine···acetaldehyde are also included in the figure. The N···C is larger in the pyridine···acetone and pyridine···2-butanone complexes than in pyridine···formaldehyde and pyridine···acetaldehyde ones. On the contrary, the CH···O distance decreases as the carbonyl molecules is larger. The dissociation energy of the complexes is similar for the two smallest complexes (15.9 kJ mol^{-1}) and for the two largest, it increases with the size of the carbonyl derivative up to 19.0 kJ mol^{-1} in pyridine···2-butanone. CCSD/6-311++G(2d,p) optimized geometries. The dissociation energy, D_e, has been obtained at CCSD(T)/6-311++G(2d,p)//CCSD/6-311++G(2d,p) computational level including the BSSE correction.



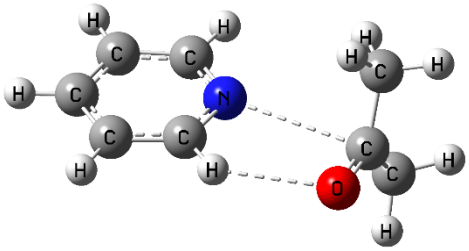
N···C = 2.865 Å, H···O = 2.534 Å

D_e = 15.9 kJ mol^{-1}



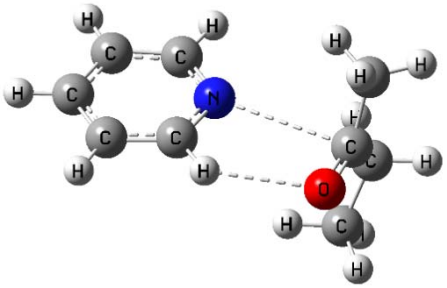
N···C = 3.012 Å, H···O = 2.479 Å

D_e = 15.9 kJ mol^{-1}



N···C = 3.118 Å, H···O = 2.439 Å

D_e = 17.2 kJ mol^{-1}



N···C = 3.095 Å, H···O = 2.435 Å

D_e = 19.0 kJ mol^{-1}

Figure S4. The MP2/6-311++G(2d,p) relaxed scan bidimensional potential energy function for the internal rotations of the two methyl tops for pyridine···acetone (α=∠H_{17}-C_{14}-C_{12}-O_{13}, α'=∠H_{20}-C_{15}-C_{12}-O_{13}, see figure in Table S8 for the atom labelling). Below, the monodimensional energy profile is shown. The interaction of acetone with pyridine alters the form of the potential energy function around the minima as well as the phase of the potential energy function.

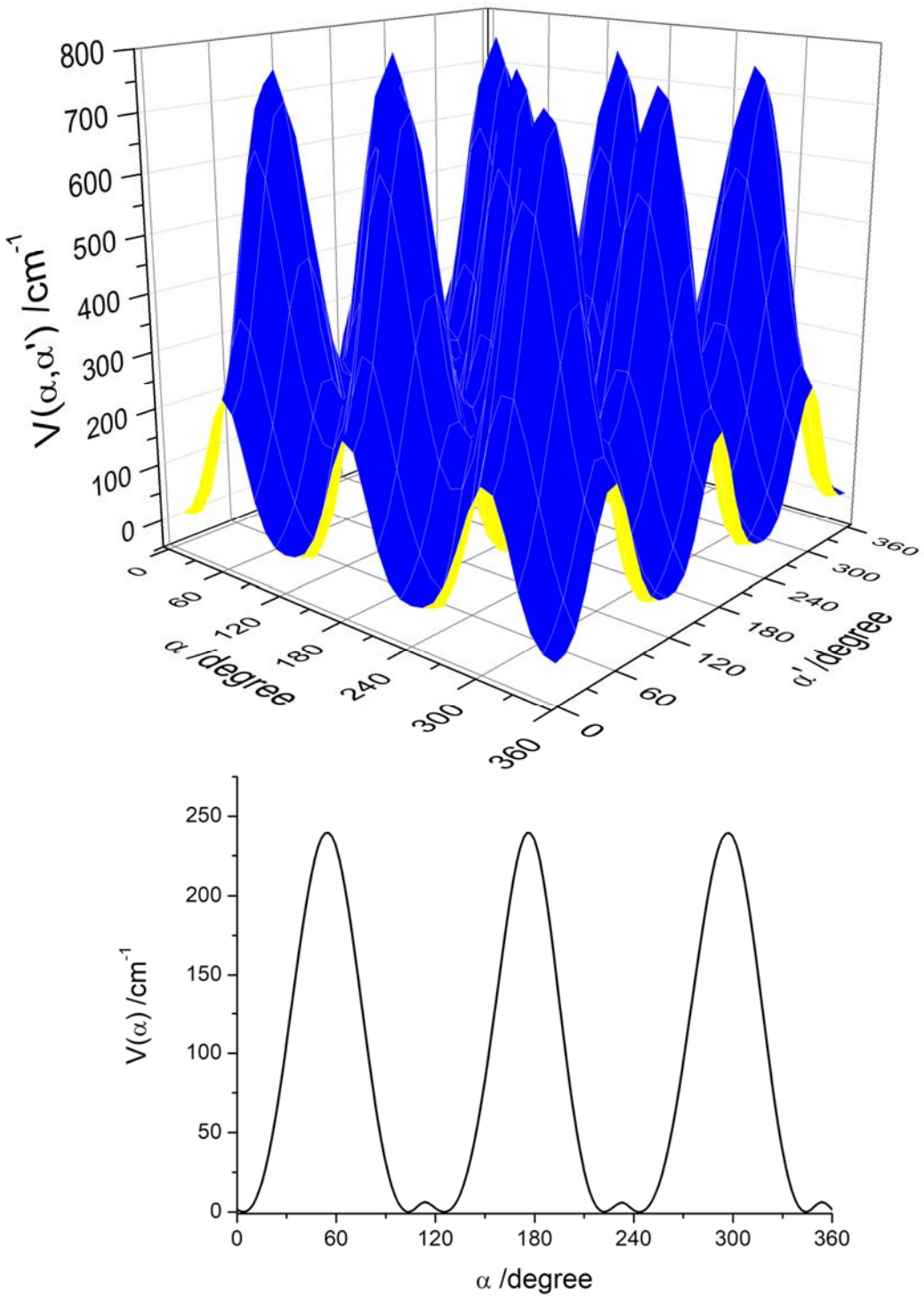


Figure S5. (a) The MP2/6-311++G(2d,p) internal rotation potential energy function of pyridine···acetone (black), free acetone (red), and comparison of their difference (blue) with the predicted dependence of r(N···C) Bürgi-Dunitz distance (green). The phase relationships between the difference function and the r(N···C) distance evidences that the $n \rightarrow \pi^*$ tetrel bond might contribute to alter the internal rotation potential energy function and thus the barrier. (b) the same for pyridine···2-butanone.

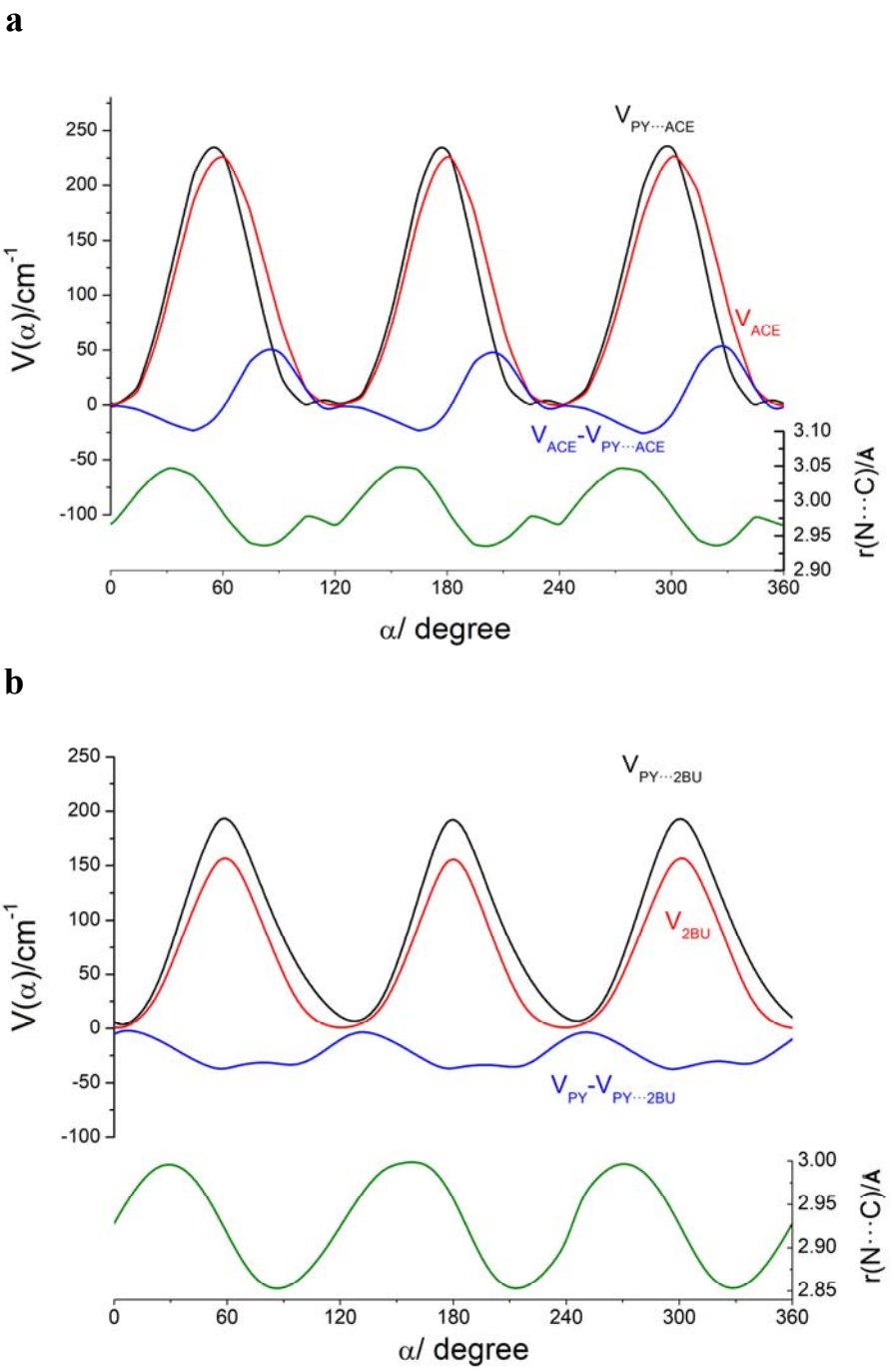


Figure S6. Exponential relationship between ρBCP (au) and the interatomic distance (Å) between pyridine and FA: formaldehyde; AC: Acetaldehyde; ACE: Acetone; 2BU: 2-butanone.

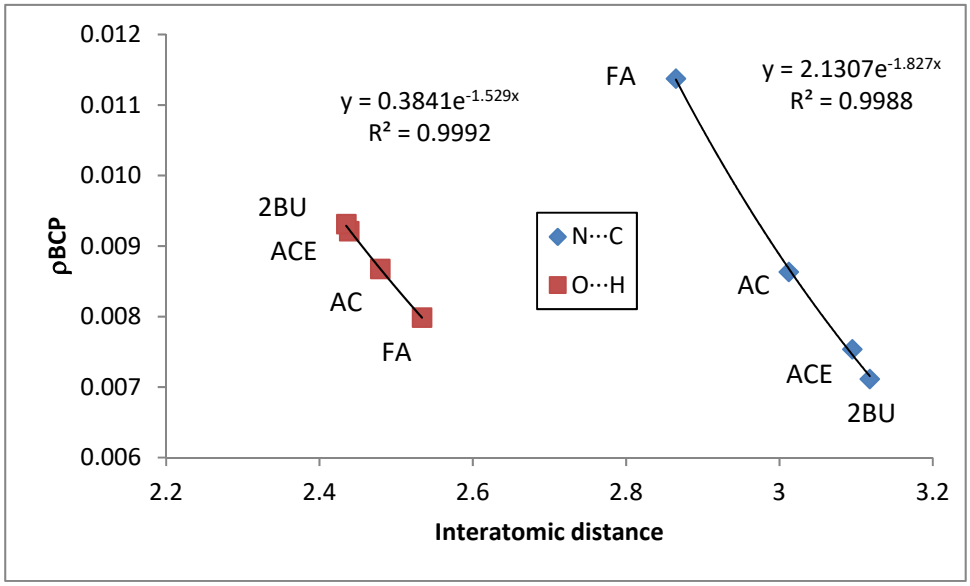
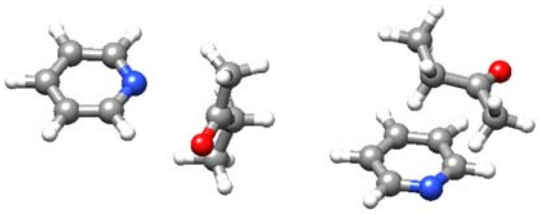


Table S1. Spectroscopic parameters and energies calculated for the lowest energy forms, labelled A and B, found for the pyridine···2-butanone adduct at B3LYP-D3BJ/6-311++G(2d,p) level and their comparison with the experimental values.

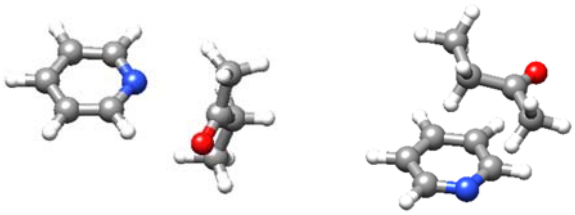
Parameters[a]	A	B	exp.
A/MHz	1886.3	1531.4	1886.3549(12)[b]
B/MHz	551.7	779.8	540.40496(22)
C/MHz	546.4	679.7	535.87643(24)
P_{aa}/μÅ^2	786.5	530.8	805.18171(49)
P_{bb}/μÅ^2	138.4	212.7	137.90743(49)
P_{cc}/μÅ^2	129.5	117.3	130.00564(49)
χ_{ab}/MHz	-4.46	2.76	-4.0686(20)
χ_{ac}/MHz	3.23	-4.28	3.1633(29)
χ_{bc}/MHz	1.23	1.52	0.9053(29)
μ_a/D	2.2	1.6	
μ_b/D	-1.0	1.5	
μ_c/D	1.9	-2.0	
E/h	-480.9477308	-480.947584	
ΔE/kJ mol^{-1}	0.0	0.4	



[a] A, B and C are the rotational constants. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia I_α as for example $P_{cc}=(I_a+I_b-I_c)/2$. χ_{aa}, χ_{bb}, χ_{cc}, are the ^{14}N quadrupole coupling constants. μ_a, μ_b *and* μ_c are the electric dipole moment components (in Debye) along the principal inertial axes. E are the calculated electronic energies and ΔE the energies relative to the global minimum A form. [b] Standard errors are given in parentheses in units of the last digits.

Table S2. Spectroscopic parameters and energies calculated for the lowest energy forms, labelled A and B, found for the pyridine···2-butanone adduct at MP2/6-311++G(2d,p) level and their comparison with the experimental values.

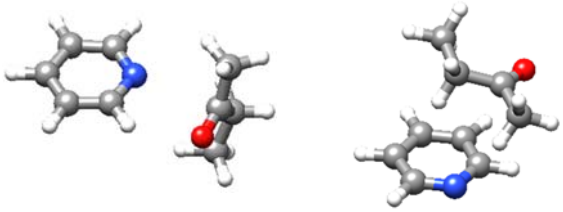
Parameters[a]	A	B	exp.
A/MHz	1893.4	1531.4	1886.3549(12)[b]
B/MHz	565.6	815.1	540.40496(22)
C/MHz	560.7	705.6	535.87643(24)
P_{aa}/μÅ^2	764.0	503.1	805.18171(49)
P_{bb}/μÅ^2	137.3	213.1	137.90743(49)
P_{cc}/μÅ^2	129.6	116.9	130.00564(49)
χ_{ab}/MHz	-4.38	2.70	-4.0686(20)
χ_{ac}/MHz	3.10	-3.77	3.1633(29)
χ_{bc}/MHz	1.28	1.07	0.9053(29)
μ_a/D	2.3	1.3	
μ_b/D	0.8	1.5	
μ_c/D	-1.9	-1.6	
E/h	-479.5663233	-479.5670042	
ΔE/kJmol^{-1}	0.0	1.8	



[a] A, B and C are the rotational constants. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia I_α as for example $P_{cc}=(I_a+I_b-I_c)/2$. χ_{aa}, χ_{bb}, χ_{cc}, are the ^{14}N quadrupole coupling constants. μ_a, μ_b *and* μ_c are the electric dipole moment components (in Debye) along the principal inertial axes. E are the calculated electronic energies and ΔE the energies relative to the global minimum A form.
[b] Standard errors are given in parentheses in units of the last digits.

Table S3. Spectroscopic parameters and energies calculated for the lowest energy forms, A and B, found for the pyridine···2-butanone adduct at CCSD/6-311++G(2d,p) level and their comparison with the experimental values. The energies calculated at CCSD(T)/6-311++G(2d,p) level for the CCSD geometries are given.

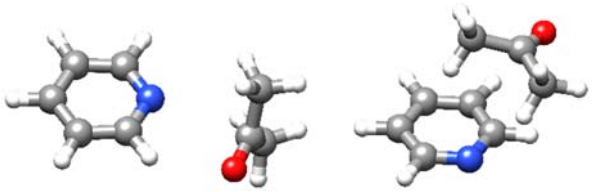
Parameters[a]	A	B	Exp.
A/MHz	1891.2	1526.0	1886.3549(12)[b]
B/MHz	539.2	756.3	540.40496(22)
C/MHz	533.7	661.6	535.87643(24)
P_{aa}/μÅ^2	808.5	550.5	805.18171(49)
P_{bb}/μÅ^2	138.4	213.4	137.90743(49)
P_{cc}/μÅ^2	128.8	117.8	130.00564(49)
χ_{aa}/MHz	-4.47	2.87	-4.0686(20)
χ_{bb}/MHz	2.95	-3.90	3.1633(29)
χ_{cc}/MHz	1.52	1.02	0.9053(29)
μ_a/D	2.2	-1.2	
μ_b/D	-1.0	1.5	
μ_c/D	1.8	1.7	
E/h	-479.629065	-479.6281605	
ΔE/kJmol^{-1}	0.00	2.4	
$E_{CCSD(T)}$/h	-479.713866	-479.713345	
$\Delta E_{CCSD(T)}$/kJmol^{-1}	0.00	1.4	
D_e (BSSE) $_{CCSD(T)}$/kJmol^{-1}	19.0	16.5	



[a] A, B and C are the rotational constants. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia I_α as for example $P_{cc}=(I_a+I_b-I_c)/2$. χ_{aa}, χ_{bb}, χ_{cc}, are the ^{14}N quadrupole coupling constants. μ_a, μ_b *and* μ_c are the electric dipole moment components (in Debye) along the principal inertial axes. E are the calculated electronic energies, ΔE the energies relative to the global minimum A form and D_e (BSSE) dissociation energy calculated using counterpoise procedure (S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566). [b] Standard errors are given in parentheses in units of the last digits.

Table S4. Spectroscopic parameters and energies calculated for the lowest energy forms, A and B, found for the pyridine···acetone adduct at B3LYP-D3BJ/6-311++G(2d,p) level and their comparison with the experimental values.

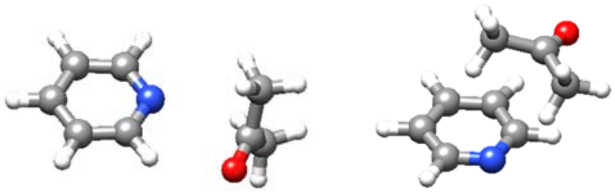
Parameters[a]	A	B	exp.
A/MHz	2727.1	2142.2	2722.6132(14)[b]
B/MHz	635.5	833.0	627.32259(26)
C/MHz	581.7	787.7	575.35390(23)
P_{aa}/μÅ^2	739.4	506.2	749.18477(39)
P_{bb}/μÅ^2	129.5	135.4	129.19479(39)
P_{cc}/μÅ^2	55.9	100.5	56.42802(39)
χ_{ab}/MHz	-4.53	1.79	-4.1442(86)
χ_{ac}/MHz	0.93	-3.45	0.8378(91)
χ_{bc}/MHz	3.60	1.66	3.3064(91)
μ_a/D	2.1	1.9	
μ_b/D	-2.2	0.2	
μ_c/D	0.1	2.5	
E/h	-441.6163804		
ΔE/kJmol^{-1}	0.0	0.5	



[a] A, B and C are the rotational constants. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia I_α as for example $P_{cc}=(I_a+I_b-I_c)/2$. χ_{aa}, χ_{bb}, χ_{cc}, are the ^{14}N quadrupole coupling constants. μ_a, μ_b *and* μ_c are the electric dipole moment components (in Debye) along the principal inertial axes. E are the calculated electronic energies and ΔE the energies relative to the global minimum A form. [b] Standard errors are given in parentheses in units of the last digits.

Table S5. Spectroscopic parameters and energies calculated for the lowest energy forms, A and B, found for the pyridine···acetone adduct at MP2/6-311++G(2d,p) level and their comparison with the experimental values.

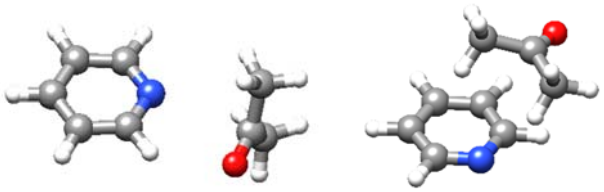
Parameters[a]	A	B	exp.
A/MHz	2722.1	2134.9	2722.6132(14)[b]
B/MHz	659.4	870.8	627.32259(26)
C/MHz	600.9	819.0	575.35390(23)
P_{aa}/μÅ^2	710.9	480.4	749.18477(39)
P_{bb}/μÅ^2	130.1	136.7	129.19479(39)
P_{cc}/μÅ^2	55.5	100.0	56.42802(39)
χ_{ab}/MHz	-4.40	2.05	-4.1442(86)
χ_{ac}/MHz	0.98	-4.06	0.8378(91)
χ_{bc}/MHz	3.42	2.01	3.3064(91)
μ_a/D	2.2	1.55	
μ_b/D	-2.2	-0.15	
μ_c/D	0.2	2.19	
E/h	-440.3615441	-440.3621202	
ΔE/kJmol^{-1}	0.0	-1.5	



[a] A, B and C are the rotational constants. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia I_α as for example $P_{cc}=(I_a+I_b-I_c)/2$. χ_{aa}, χ_{bb}, χ_{cc}, are the ^{14}N quadrupole coupling constants. μ_a, μ_b *and* μ_c are the electric dipole moment components (in Debye) along the principal inertial axes. E are the calculated electronic energies and ΔE the energies relative to the global minimum A form.
[b] Standard errors are given in parentheses in units of the last digits.

Table S6. Spectroscopic parameters and energies calculated for the lowest energy forms, A and B, found for the pyridine···acetone adduct at CCSD/6-311++G(2d,p) level and their comparison with the experimental values. The energies calculated at CCSD(T)/6-311++G(2d,p) level for the CCSD geometries are given.

Parameters[a]	A	B	Exp.
A/MHz	2722.8	2137.7	2722.6132(14)[b]
B/MHz	630.4	809.7	627.32259(26)
C/MHz	577.3	765.8	575.35390(23)
P_{aa}/μÅ^2	745.7	523.8	749.18477(39)
P_{bb}/μÅ^2	129.7	136.1	129.19479(39)
P_{cc}/μÅ^2	55.9	100.3	56.42802(39)
χ_{aa}/MHz	-4.47	2.04	-4.1442(86)
χ_{bb}/MHz	0.94	-3.97	0.8378(91)
χ_{cc}/MHz	3.53	1.93	3.3064(91)
μ_a/D	-2.1	1.5	
μ_b/D	-2.2	-0.1	
μ_c/D	-0.1	-2.3	
E/h	-440.4136567	-440.4128049	
ΔE/kJmol^{-1}	0.0	2.2	
$E_{CCSD(T)}$/h	-479.71386599	-479.71334506	
$\Delta E_{CCSD(T)}$/kJmol^{-1}	0.00	1.3	
D_e (BSSE) $_{CCSD(T)}$/kJmol^{-1}	17.2	15.1	



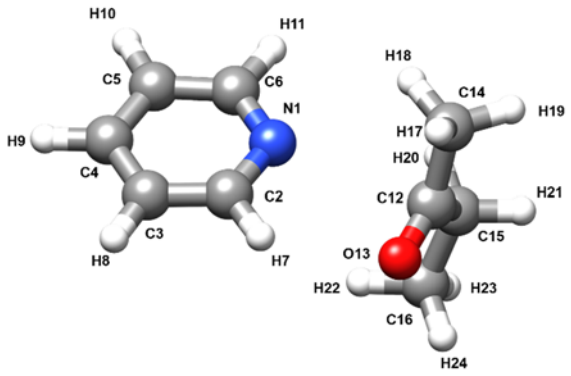
[a] A, B and C are the rotational constants. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia I_α as for example $P_{cc}=(I_a+I_b-I_c)/2$. χ_{aa}, χ_{bb}, χ_{cc}, are the ^{14}N quadrupole coupling constants. μ_a, μ_b *and* μ_c are the electric dipole moment components (in Debye) along the principal inertial axes. E are the calculated electronic energies, ΔE the energies relative to the global minimum A form and D_e (BSSE) dissociation energy calculated using counterpoise procedure (S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566). [b] Standard errors are given in parentheses in units of the last digits.

Table S7. Rotational parameters obtained from the independent semirigid rotor analysis of the *A* and *E* methyl torsion states of the pyridine···2-butanone adduct and their comparison with the CCSD/6-311++G(2d,p) *ab initio* constants for the most stable form of the complex (see Figure 3 and Tables S1-S3)

Fitted Parameters[a]	*A*	*E*	*Ab initio*
A/MHz	1886.3520(16)[b]	1886.300(16)	1891.2
B/MHz	540.44497(20)	540.3406(24)	539.2
C/MHz	535.89541(19)	535.8058(74)	533.7
D_J/kHz	0. 2252(18)	0. 2129(86)	
D_{JK}/kHz	2.216(15)	-70.2(46)	
D_K/kHz	-1.34(35)	[0.]	
d_1/kHz	-0.0059(14)	-0.103(30	
d_2/kHz	0.00937(75)	-3.6(13)	
D_a/*MHz*	-	2.033(42)	
D_b/*MHz*	-	7.72(64)	
1.5(χ_{aa})/MHz	-6.1036(49)	-6.1005(76)	-6.70
0.25(χ_{bb}-χ_{cc}) /MHz	0.5639(14)	0.5634(27)	0.36
N	168	75	
σ/kHz	5.7	6.0	

[a] *A*, *B,* and *C* are rotational constants. D_J, D_{JK}, D_K, d_1, d_2 are quartic centrifugal distortion constants. D_a and D_b are the coefficients of angular momentum perturbation operators ($D_a\mathbf{P}_a$, $D_b\mathbf{P}_b$) needed to account for the deviations of the E rotational transitions from the semirigid rotor behavior. χ_{aa}, $\chi_{bb,}$ and χ_{cc} are ^{14}N nuclear quadrupole coupling constants. N is the number of hyperfine quadrupole components fitted. σ is the rms deviation of the fit. [b] Standard errors are given in parentheses in units of the last digit.

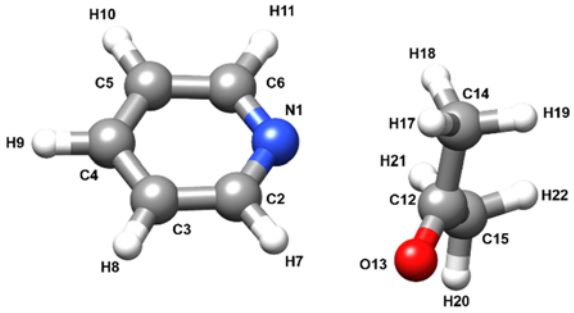
Table S8. Optimized geometry (Å) and energy (hartree) at CCSD/6-311++G(2d,p) computational level for pyridine···2-butanone A form.



E(CCSD): -479.6290657

N1, -0.745279,-0.084724,-0.412211
C2, -1.104021, 0.551879, 0.711018
C3, -2.427009, 0.672639, 1.136003
C4, -3.433361, 0.104771, 0.359986
C5, -3.074628,-0.560451,-0.809906
C6, -1.724353,-0.625841,-1.148236
H7, -0.292131, 0.980880, 1.291381
H8, -2.654451, 1.200934, 2.055826
H9, -4.474437, 0.178489, 0.659343
H10,-3.820181,-1.020553,-1.449819
H11,-1.412833,-1.138564,-2.055366
C12, 2.283684, 0.481307,-0.123394
O13, 2.121158, 0.986321, 0.968509
C14, 2.315569, 1.314445,-1.387720
C15, 2.489309,-1.012560,-0.298671
C16, 2.207307,-1.820001, 0.962756
H17, 2.336330, 2.375606,-1.136486
H18, 1.417757, 1.093425,-1.972564
H19, 3.187451, 1.056598,-1.997663
H20, 1.856757,-1.340102,-1.130618
H21, 3.527753,-1.152587,-0.630528
H22, 1.162687,-1.706137, 1.262377
H23, 2.404043,-2.882378, 0.791354
H24, 2.832235,-1.479599, 1.791457

Table S9. Optimized geometry (Å) and energy (hartree) at CCSD/6-311++G(2d,p) computational level for pyridine···acetone A form.



E(CCSD) = -440.4136567

N1, -0.540070,-0.418384, 0.018156
C2, -0.879347, 0.878039, 0.015902
C3, -2.200246, 1.326061, 0.007497
C4, -3.225918, 0.385228, 0.000767
C5, -2.887727,-0.965855, 0.003022
C6, -1.537820,-1.311595, 0.011608
H7, -0.053518, 1.583533, 0.021057
H8, -2.411170, 2.390202, 0.006136
H9, -4.265970, 0.696882,-0.005661
H10,-3.648697,-1.739114,-0.001973
H11,-1.242536,-2.358311, 0.013542
C12, 2.530073, 0.123899,-0.008617
O13, 2.371472, 1.326482, 0.035454
C14, 2.574028,-0.626455,-1.323040
C15, 2.722383,-0.701830, 1.245628
H16, 2.238965, 0.020736,-2.133987
H17, 1.945104,-1.518448,-1.271228
H18, 3.603872,-0.948190,-1.517117
H19, 2.802129,-0.049372, 2.115671
H20, 1.862390,-1.367660, 1.361610
H21, 3.620628,-1.322383, 1.159401

Table S10. Electron density properties (au) at the intermolecular BCPs at CCSD/6-311++G(2d,p) computational level for the complexes pyridine···formaldehyde (PY···FA), pyridine···acetaldehyde (PY···AC), pyridine···acetone (PY···ACE) and pyridine···2-butanone (PY···2BU)

Complex	Contact	ρ	$\nabla^2 \rho$	H
PY···FA	N···C	0.0114	0.0397	0.0015
PY···FA	O···H	0.0080	0.0284	0.0010
PY···AC	N···C	0.0086	0.0306	0.0013
PY···AC	O···H	0.0087	0.0306	0.0010
PY···ACE	N···C	0.0071	0.0257	0.0011
PY···ACE	O···H	0.0092	0.0327	0.0011
PY···2BU	N···C	0.0075	0.0269	0.0011
PY···2BU	O···H	0.0093	0.0332	0.0011

Table S11. Observed rotational frequencies for the conformer A of the pyridine···2-butanone complex.

J K$_-$K$_+$	J`K`$_-$K`$_+$	Sym	F	F`	obs/MHz	Err/MHz	obs-calc/MHz
2 1 2	1 1 1	A	2	1	2147.103	0.015	0.005
			1	1	2147.559	0.015	0.008
			2	2	2148.051	0.015	0.005
			3	2	2148.341	0.015	0.003
			1	0	2149.913	0.015	-0.010
2 0 2	1 0 1	A	2	2	2151.440	0.015	-0.002
			1	0	2151.645	0.015	0.001
			2	1	2152.655	0.015	-0.007
			3	2	2152.748	0.015	0.000
			1	1	2154.692	0.015	-0.003
2 0 2	1 0 1	E	2	2	2150.968	0.015	0.000
			1	0	2151.177	0.015	0.007
			2	1	2152.188	0.015	0.000
			3	2	2152.276	0.015	0.001
			1	1	2154.216	0.015	-0.004
2 1 1	1 1 0	A	3	2	2157.485	0.015	0.000
			1	1	2157.780	0.015	0.002
			1	2	2158.057	0.015	0.007
			1	0	2158.462	0.015	0.005
2 1 1	1 1 0	E	2	1	2155.607	0.030	-0.027
1 1 0	0 0 0	A	0	1	2426.338	0.015	-0.005
			2	1	2426.748	0.015	-0.002
			1	1	2427.019	0.015	-0.003
1 1 0	0 0 0	E	1	1	2427.893	0.030	0.021
4 0 4	3 1 2	A	3	2	2943.221	0.015	0.002
			5	4	2943.358	0.015	0.006
4 0 4	3 1 2	E	3	2	2940.789	0.015	-0.005
			5	4	2940.930	0.015	0.005
3 1 3	2 1 2	A	3	3	3221.607	0.015	-0.001
			4	3	3222.251	0.015	0.003
			2	1	3222.308	0.015	-0.002
3 1 3	2 1 2	E	3	3	3221.607	0.015	0.002
			4	3	3222.251	0.015	0.001
			2	1	3222.308	0.015	0.002
3 0 3	2 0 2	A	3	3	3227.650	0.015	0.004
			2	1	3228.744	0.030	-0.002
			2	1	3228.744	0.030	-0.002
			3	2	3228.953	0.015	0.001
			4	3	3228.989	0.015	-0.009
			2	2	3230.781	0.015	0.002
3 0 3	2 0 2	E	3	3	3226.936	0.015	0.000
			2	1	3228.037	0.015	0.000
			3	2	3228.243	0.015	0.000
			4	3	3228.280	0.015	-0.009
			3	3	3226.936	0.015	-0.001
			2	2	3230.071	0.015	0.001
3 2 2	2 2 1	A	3	3	3229.219	0.030	-0.013
3 2 1	2 2 0	A	3	3	3229.281	0.030	0.004
			4	3	3229.281	0.030	0.001
3 1 2	2 1 1	A	3	3	3234.527	0.015	-0.002
			3	2	3235.545	0.015	0.000
			2	1	3235.843	0.015	-0.001
			4	3	3235.922	0.015	0.000
			2	2	3237.432	0.015	0.006
3 1 2	2 1 1	E	3	3	3234.317	0.015	-0.008
			3	2	3235.321	0.015	-0.006
			2	1	3235.635	0.015	-0.008
			4	3	3235.709	0.015	-0.005

3	1	2	2	1	1	E	2	2	3237.189	0.030	-0.014
2	1	2	1	0	1	A	3	2	3493.884	0.015	0.001
2	1	1	1	0	1	A	1	0	3506.423	0.015	-0.003
							2	2	3506.673	0.015	-0.002
							3	2	3507.690	0.015	-0.002
							2	1	3507.892	0.015	-0.004
							1	1	3509.476	0.015	-0.001
2	1	1	1	0	1	E	1	0	3506.937	0.015	0.007
							2	2	3507.205	0.015	0.004
							3	2	3508.208	0.015	0.005
							2	1	3508.427	0.015	0.005
							1	1	3509.982	0.015	0.001
7	1	6	6	2	4	A	8	7	3552.588	0.030	-0.007
							6	5	3552.665	0.030	-0.009
7	1	6	6	2	4	E	8	7	3549.715	0.030	0.021
							6	5	3549.791	0.030	0.016
8	2	7	8	1	7	A	7	7	3962.177	0.015	0.001
							9	9	3962.250	0.015	0.002
							8	8	3962.831	0.015	0.003
7	2	6	7	1	6	A	6	6	3980.366	0.015	0.000
							8	8	3980.457	0.015	0.000
							7	7	3981.085	0.015	0.001
6	2	5	6	1	5	A	5	5	3996.279	0.015	-0.003
							7	7	3996.398	0.015	-0.001
							6	6	3997.095	0.015	-0.003
5	2	4	5	1	4	A	4	4	4009.894	0.015	-0.005
							6	6	4010.064	0.015	-0.001
5	0	5	4	1	3	A	4	3	4010.183	0.015	-0.004
							6	5	4010.306	0.015	0.002
							5	4	4010.466	0.015	-0.001
5	0	5	4	1	3	E	4	3	4006.750	0.015	-0.003
							6	5	4006.868	0.015	-0.002
							5	4	4007.028	0.015	-0.003
5	2	4	5	1	4	A	5	5	4010.878	0.015	0.001
4	2	3	4	1	3	A	3	3	4021.176	0.015	-0.003
							5	5	4021.440	0.015	0.002
							4	4	4022.451	0.015	0.004
3	2	1	3	1	3	A	4	4	4058.052	0.015	0.011
							3	3	4058.684	0.030	0.005
							4	3	4058.684	0.030	0.002
							2	3	4058.684	0.030	0.001
4	2	2	4	1	4	A	3	3	4067.252	0.015	-0.002
							5	5	4067.319	0.015	0.006
							4	4	4067.553	0.015	0.007
4	1	4	3	1	3	A	4	3	4296.066	0.015	0.002
							5	4	4296.226	0.015	0.010
							3	3	4297.062	0.015	0.001
4	2	3	3	2	2	A	4	3	4304.818	0.030	0.004
							4	4	4304.818	0.030	0.004
							5	4	4305.372	0.015	0.003
4	2	2	3	2	1	A	4	4	4304.931	0.030	0.002
							4	3	4304.931	0.030	-0.001
							5	4	4305.494	0.015	0.006
							3	2	4305.631	0.030	0.000
							3	3	4305.631	0.030	-0.005
4	0	4	3	0	3	A	4	4	4303.838	0.015	0.000
							3	2	4305.099	0.015	-0.002
							5	4	4305.222	0.015	0.003
							3	3	4306.919	0.015	-0.008
4	0	4	3	0	3	E	4	4	4302.893	0.015	-0.004
							3	2	4304.159	0.015	-0.001

4 0 4	3 0 3	E	4	3	4304.248	0.015	-0.003
			5	4	4304.280	0.015	0.001
4 1 3	3 1 2	A	4	4	4312.862	0.015	-0.004
			4	3	4314.263	0.015	0.005
			3	2	4314.345	0.015	0.002
			5	4	4314.430	0.015	0.001
			3	3	4316.225	0.015	0.001
4 1 3	3 1 2	E	4	4	4312.700	0.015	-0.006
			4	3	4314.094	0.015	-0.001
			3	2	4314.182	0.015	-0.001
			5	4	4314.263	0.015	-0.004
			3	3	4316.057	0.015	-0.001
3 1 2	2 0 2	A	3	3	4589.472	0.015	0.001
			2	1	4590.623	0.015	-0.004
			3	2	4590.775	0.015	-0.003
			4	3	4590.863	0.015	-0.002
			2	2	4592.663	0.015	0.004
3 1 2	2 0 2	E	3	3	4590.260	0.015	0.006
			2	1	4591.404	0.015	0.000
			3	2	4591.561	0.015	0.000
			4	3	4591.644	0.015	0.001
			2	2	4593.430	0.015	-0.006
6 0 6	5 1 4	A	5	4	5074.727	0.015	-0.008
			7	6	5074.837	0.015	0.003
			6	5	5075.081	0.015	0.001
6 0 6	5 1 4	E	5	4	5070.094	0.015	0.011
			7	6	5070.187	0.015	0.004
			6	5	5070.425	0.015	-0.002
5 1 5	4 1 4	A	5	5	5369.307	0.015	0.003
			5	4	5370.099	0.015	0.003
			6	5	5370.187	0.015	0.009
			4	4	5371.159	0.015	0.010
5 1 5	4 1 4	E	5	5	5369.116	0.030	-0.007
			5	4	5369.927	0.030	0.010
			6	5	5370.015	0.030	0.016
5 0 5	4 0 4	A	6	5	5381.393	0.030	0.012
			4	3	5381.300	0.030	-0.010
			4	4	5383.045	0.015	-0.001
5 0 5	4 0 4	E	4	3	5380.143	0.015	0.001
			6	5	5380.221	0.015	0.009
5 2 3	4 2 2	A	6	5	5381.783	0.030	-0.013
			4	3	5381.838	0.030	0.011
5 1 4	4 1 3	A	5	4	5392.831	0.030	-0.007
			4	3	5392.880	0.030	0.013
			6	5	5392.932	0.015	0.001
5 1 4	4 1 3	E	5	4	5392.656	0.030	-0.008
			4	3	5392.704	0.030	0.010
			6	5	5392.756	0.015	-0.002
4 1 3	3 0 3	A	4	3	5676.085	0.015	-0.001
			3	2	5676.221	0.030	-0.003
			5	4	5676.293	0.030	-0.002
4 1 3	3 0 3	E	4	3	5677.411	0.015	-0.002
			3	2	5677.548	0.030	-0.001
			5	4	5677.621	0.030	-0.001
6 1 6	5 1 5	A	6	5	6444.057	0.015	-0.003
			7	6	6444.116	0.015	0.007
6 1 6	5 1 5	E	6	5	6443.838	0.015	0.000
6 0 6	5 0 5	A	6	5	6457.445	0.030	-0.006
			7	6	6457.445	0.030	-0.017
6 0 6	5 0 5	E	6	5	6456.062	0.030	0.003
			7	6	6456.062	0.030	-0.009

6 2 5	5 2 4	A	7	6	6457.740	0.015	0.001
6 2 4	5 2 3	A	6	5	6457.980	0.015	-0.002
			5	4	6458.149	0.030	-0.008
			7	6	6458.149	0.030	-0.008
6 1 5	5 1 4	A	6	5	6471.350	0.030	0.004
			5	4	6471.350	0.030	-0.006
			7	6	6471.390	0.030	-0.014
6 1 5	5 1 4	E	6	5	6471.146	0.030	0.010
			5	4	6471.146	0.030	0.000
			7	6	6471.193	0.030	-0.001
5 1 4	4 0 4	A	5	4	6763.728	0.015	-0.005
			4	3	6764.008	0.030	0.017
			6	5	6764.008	0.030	0.000
5 1 4	4 0 4	E	5	4	6765.824	0.015	-0.002
			4	3	6766.103	0.030	0.020
			6	5	6766.103	0.030	0.002
3 2 1	2 1 1	A	2	1	7265.915	0.015	-0.001
			4	3	7266.475	0.015	-0.005
			3	2	7267.496	0.015	0.003
3 2 2	2 1 2	A	2	1	7280.062	0.015	-0.005
			4	3	7280.221	0.030	-0.007
			3	3	7280.221	0.030	-0.007
			2	3	7280.221	0.030	-0.007
			3	2	7280.515	0.030	-0.005
			2	2	7280.515	0.030	-0.005
5 2 3	5 1 5	A	4	4	4078.925	0.030	-0.002
			6	6	4078.925	0.030	-0.007
6 2 4	6 1 6	A	6	6	4092.881	0.030	0.006
			7	7	4092.975	0.030	-0.005
7 2 5	7 1 7	A	7	7	4109.360	0.015	0.006
			8	8	4109.539	0.015	-0.003
5 2 3	4 2 2	A	5	4	5381.508	0.015	0.004
5 2 4	4 2 3	A	4	3	5381.588	0.015	0.001
5 3 3	4 3 2	A	6	5	5381.588	0.015	-0.008
7 1 7	6 1 6	A	6	5	7517.977	0.015	-0.002
7 1 7	6 1 6	E	6	5	7517.729	0.015	0.004
7 0 7	6 0 6	A	7	6	7533.451	0.030	0.014
			8	7	7533.451	0.030	0.007
7 0 7	6 0 6	E	7	6	7531.817	0.030	-0.010
			8	7	7531.817	0.030	-0.017
7 2 6	6 2 5	A	8	7	7533.889	0.015	-0.001
7 1 6	6 1 5	A	6	5	7549.794	0.030	-0.001
			7	6	7549.794	0.030	0.001
6 1 5	5 0 5	A	7	6	7854.042	0.030	0.010
			5	4	7854.042	0.030	0.006
4 2 3	3 1 3	A	3	2	8363.269	0.015	0.001
			5	4	8363.351	0.015	0.001
			4	3	8363.433	0.015	-0.003
8 1 8	7 1 7	A	9	8	8591.822	0.015	-0.008
8 0 8	7 0 7	A	8	7	8609.311	0.030	0.003
			9	8	8609.311	0.030	-0.001
8 0 8	7 0 7	E	8	7	8607.482	0.030	-0.001
			9	8	8607.482	0.030	-0.005

Table S12. Observed rotational frequencies for the conformer A of the pyridine···acetone complex.

J K_-K_+	J` $K`_-K`_+$	Sym	F	F`	obs/MHz	Err/MHz	obs-calc/MHz
2 1 1	2 0 2	EE	3	3	2200.059	0.015	-0.008
			2	2	2201.138	0.015	-0.001
3 1 2	3 0 3	EE	3	3	2282.134	0.015	0.008
			4	4	2281.350	0.015	0.002
4 1 3	4 0 4	EE	5	5	2393.011	0.015	0.011
			4	4	2393.671	0.015	0.001
			3	3	2392.830	0.015	0.001
2 0 2	1 0 1	EE	3	2	2404.435	0.015	0.002
			2	1	2404.328	0.015	-0.006
2 1 1	1 1 0	EE	3	2	2457.476	0.015	0.003
			2	1	2456.223	0.015	0.010
2 1 1	1 1 0	AE	3	2	2457.197	0.015	0.006
1 1 1	0 0 0	AA	2	1	3297.983	0.015	0.002
1 1 1	0 0 0	EE	1	1	3298.086	0.015	-0.003
			2	1	3297.842	0.015	0.006
3 1 3	2 1 2	AA	4	3	3529.849	0.015	-0.001
			3	2	3529.470	0.015	0.008
3 1 3	2 1 2	EE	4	3	3529.702	0.015	-0.001
			2	1	3529.620	0.015	0.000
			3	2	3529.318	0.015	0.002
3 0 3	2 0 2	AA	4	3	3604.474	0.015	0.001
			3	2	3604.408	0.015	-0.001
3 0 3	2 0 2	EE	4	3	3604.166	0.015	0.002
			3	2	3604.098	0.015	-0.002
			2	1	3603.909	0.015	-0.002
			3	3	3602.747	0.015	-0.011
3 0 3	2 0 2	AE	4	3	3603.969	0.015	-0.005
			3	2	3603.909	0.015	0.000
3 0 3	2 0 2	EA	4	3	3603.741	0.015	0.005
			3	2	3603.676	0.015	0.004
3 1 2	2 1 1	AA	4	3	3685.624	0.015	0.005
			3	2	3685.264	0.015	0.003
3 1 2	2 1 1	EE	2	1	3685.515	0.015	0.001
			4	3	3685.446	0.015	0.002
			3	2	3685.084	0.015	-0.002
5 0 5	4 1 4	AA	6	5	4121.310	0.015	-0.005
5 0 5	4 1 4	EE	5	4	4120.379	0.015	0.003
			6	5	4120.255	0.015	0.004
			4	3	4120.147	0.015	0.007
5 0 5	4 1 4	AE	6	5	4120.464	0.015	0.006
2 1 2	1 0 1	AA	3	2	4448.857	0.015	0.004
2 1 2	1 0 1	EE	2	1	4448.958	0.015	0.010
			3	2	4448.773	0.015	0.005
			2	2	4447.697	0.015	-0.008
			1	0	4447.498	0.015	0.005
			1	1	4450.594	0.015	-0.007
4 1 4	3 1 3	AA	5	4	4705.259	0.015	0.001
			3	2	4705.166	0.015	-0.003
4 1 4	3 1 3	EE	5	4	4705.050	0.015	-0.009
			3	2	4704.964	0.015	-0.006
			4	3	4704.876	0.015	-0.004
4 1 4	3 1 3	AE	4	3	4704.465	0.015	0.007
			3	2	4704.550	0.015	0.001
			5	4	4704.636	0.015	-0.001
4 0 4	3 0 3	AA	3	2	4801.354	0.015	0.001

4 0 4	3 0 3	AA	4	3	4801.417	0.030	-0.001
			5	4	4801.465	0.030	-0.005
4 0 4	3 0 3	EE	3	2	4800.927	0.015	0.000
			4	3	4800.998	0.030	0.006
			5	4	4801.041	0.030	-0.003
4 0 4	3 0 3	AE	3	2	4800.690	0.015	-0.005
			4	3	4800.761	0.030	0.000
			5	4	4800.810	0.030	-0.003
4 0 4	3 0 3	EA	3	2	4800.304	0.015	-0.002
			4	3	4800.372	0.030	0.000
			5	4	4800.415	0.030	-0.009
4 1 3	3 1 2	AA	4	3	4912.761	0.015	0.003
			5	4	4912.923	0.015	0.005
4 1 3	3 1 2	EE	5	4	4912.699	0.015	0.002
			4	3	4912.537	0.015	0.001
4 1 3	3 1 2	EA	4	3	4912.254	0.015	0.001
			5	4	4912.414	0.015	0.000
6 0 6	5 1 5	AA	6	5	5425.025	0.015	-0.010
			7	6	5424.857	0.015	0.002
			5	4	5424.769	0.015	0.005
6 0 6	5 1 5	EE	6	5	5423.492	0.015	0.007
			7	6	5423.309	0.015	0.004
			5	4	5423.223	0.015	0.009
6 0 6	5 1 5	AE	5	4	5423.743	0.015	-0.001
			7	6	5423.835	0.015	0.000
			6	5	5424.022	0.015	0.007
6 0 6	5 1 5	EA	5	4	5419.583	0.015	-0.007
			7	6	5419.682	0.015	0.001
			6	5	5419.858	0.015	-0.001
3 1 3	2 0 2	EE	4	3	5574.035	0.015	-0.003
			3	2	5573.922	0.015	-0.007
			2	1	5573.795	0.015	-0.005
3 1 3	2 0 2	AE	4	3	5573.582	0.015	0.004
			3	2	5573.469	0.015	0.000
			2	1	5573.334	0.015	-0.006
3 1 3	2 0 2	EA	4	3	5574.436	0.015	0.000
			3	2	5574.328	0.015	0.001
			2	1	5574.194	0.015	-0.005
5 1 5	4 1 4	AA	5	4	5879.676	0.015	0.007
			6	5	5879.781	0.015	0.009
5 1 5	4 1 4	EE	6	5	5879.550	0.015	0.006
			4	3	5879.485	0.015	0.007
			5	4	5879.445	0.015	0.003
5 1 5	4 1 4	AE	5	4	5878.871	0.015	0.001
			4	3	5878.914	0.015	0.007
			6	5	5878.978	0.015	0.005
5 0 5	4 0 4	AA	6	5	5994.694	0.015	-0.006
			4	3	5994.614	0.015	-0.017
5 0 5	4 0 4	EE	6	5	5994.135	0.015	-0.006
			4	3	5994.062	0.015	-0.010
5 0 5	4 0 4	AE	6	5	5993.881	0.015	-0.007
5 0 5	4 0 4	EA	6	5	5993.267	0.015	-0.009
5 1 4	4 1 3	AA	5	4	6139.118	0.015	-0.001
			6	5	6139.207	0.015	-0.004
5 1 4	4 1 3	EE	5	4	6138.840	0.015	0.002
			6	5	6138.923	0.015	-0.006
4 1 4	3 0 3	AA	4	3	6674.629	0.015	-0.001
			3	2	6674.784	0.015	0.003

4 1 4	3 0 3	AA	5	4	6674.856	0.015	0.003
4 1 4	3 0 3	EE	4	3	6674.707	0.015	-0.002
			3	2	6674.856	0.015	-0.003
			5	4	6674.931	0.015	-0.001
4 1 4	3 0 3	AE	4	3	6674.017	0.015	-0.002
			3	2	6674.164	0.015	-0.005
			5	4	6674.241	0.015	-0.001
4 1 4	3 0 3	EA	4	3	6675.555	0.015	-0.002
			3	2	6675.702	0.015	-0.005
			5	4	6675.779	0.015	-0.001
7 0 7	6 1 6	AA	6	5	6738.187	0.015	-0.001
			8	7	6738.261	0.015	0.000
			7	6	6738.463	0.015	0.001
7 0 7	6 1 6	EE	7	6	6736.245	0.015	0.005
			8	7	6736.044	0.015	0.005
			6	5	6735.972	0.015	0.006
7 0 7	6 1 6	AE	6	5	6737.024	0.015	-0.002
			8	7	6737.098	0.015	-0.001
			7	6	6737.297	0.015	-0.003
7 0 7	6 1 6	EA	6	5	6730.478	0.015	0.002
			8	7	6730.550	0.015	0.001
			7	6	6730.748	0.015	-0.001
6 1 6	5 1 5	AA	7	6	7053.192	0.015	0.006
			6	5	7053.115	0.015	-0.004
6 1 6	5 1 5	EE	7	6	7052.952	0.015	-0.002
			6	5	7052.880	0.015	-0.006
6 1 6	5 1 5	AE	7	6	7052.214	0.015	-0.002
6 0 6	5 0 5	AA	7	6	7183.284	0.030	-0.028
			6	5	7183.284	0.030	0.018
6 0 6	5 0 5	EE	7	6	7182.569	0.030	-0.028
			6	5	7182.569	0.030	0.019
6 0 6	5 0 5	AE	7	6	7182.321	0.015	-0.029
			6	5	7182.321	0.015	0.018
6 0 6	5 0 5	EA	7	6	7181.390	0.030	-0.028
			6	5	7181.390	0.030	0.019
6 2 5	5 2 4	EE	7	6	7211.940	0.030	0.007
			5	4	7211.940	0.030	0.007
			6	5	7211.754	0.015	0.002
6 2 5	5 2 4	EA	6	5	7211.056	0.015	-0.003
			7	6	7211.232	0.030	-0.008
			5	4	7211.232	0.030	-0.008
6 2 4	5 2 3	AA	6	5	7244.852	0.015	-0.002
			5	4	7244.997	0.030	-0.004
			7	6	7244.997	0.030	-0.006
6 2 4	5 2 3	EE	7	6	7244.293	0.030	-0.007
			5	4	7244.293	0.030	-0.004
			6	5	7244.154	0.015	0.003
6 1 5	5 1 4	AA	7	6	7364.182	0.030	0.001
			5	4	7364.182	0.030	0.022
			6	5	7364.105	0.015	-0.017
6 1 5	5 1 4	EE	7	6	7363.831	0.030	-0.001
			5	4	7363.831	0.030	0.019
			6	5	7363.753	0.015	-0.020
6 1 5	5 1 4	AE	7	6	7363.561	0.030	-0.006
			5	4	7363.561	0.030	0.015
6 1 5	5 1 4	EA	7	6	7363.393	0.030	-0.007
			5	4	7363.393	0.030	0.014
5 1 5	4 0 4	AA	5	4	7752.884	0.015	0.003

5	1	5	4	0	4	AA	4	3	7753.162	0.030	0.028
							6	5	7753.162	0.030	0.006
5	1	5	4	0	4	EE	5	4	7753.162	0.015	0.004
							4	3	7753.443	0.030	0.032
							6	5	7753.443	0.030	0.010
5	1	5	4	0	4	AE	5	4	7752.134	0.015	0.006
							4	3	7752.414	0.030	0.033
							6	5	7752.414	0.030	0.012
5	1	5	4	0	4	EA	5	4	7754.742	0.015	0.001
							4	3	7755.029	0.030	0.036
							6	5	7755.029	0.030	0.014