

# Pyridine-acetaldehyde, a molecular balance to explore the $n \rightarrow \pi^*$ interaction.

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## ABSTRACT

The complex pyridine–acetaldehyde forms through an  $n \rightarrow \pi^*$  interaction and a C-H $\cdots$ O contact. The acetaldehyde methyl group internal rotation couples to an intermolecular motion exploring the Bürgi-Dunitz coordinate. This sort of molecular balance extracts energy from the  $n \rightarrow \pi^*$  interaction to reduce the internal rotation barrier with respect to free acetaldehyde.

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## Complete reference 29

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

## EXPERIMENTAL METHODS AND COMPUTATIONAL DETAILS.

Commercial samples of pyridine (PY) and acetaldehyde (AC) were used without further purification. The spectrum was recorded in the frequency range 2-12.5 GHz, using both a BrightSpec chirped-pulse Fourier transform microwave spectrometer (CP-FTMW, 2-8 GHz),<sup>1</sup> described elsewhere,<sup>2</sup> and a molecular-beam Fourier transform microwave spectrometer (MB-FTMW, 5-12.5 GHz).<sup>3</sup> The supersonic jet was generated by expansion of either Ne or Ar at backing pressures of about 2 bar through a 0.8 mm diameter pulsed heatable nozzle. PY was placed in the nozzle and AC in a reservoir inserted in the gas line just before the nozzle. In the CP-FTMW spectrometer the spectra were recorded in steps of 2 GHz. The length of the molecular pulses range from 700 to 900  $\mu$ s duration depending of the carrier gas used. Chirp pulses of 4  $\mu$ s were created by an arbitrary waveform generator and amplified to 20 W. The polarization signal was radiated from a horn antenna in a direction perpendicular to that of the expanding gas. A molecular transient emission spanning 40  $\mu$ s is then detected through a second horn, recorded with a digital oscilloscope and Fourier-transformed to the frequency domain. The accuracy of frequency measurements is better than 10 kHz. In the MB-FTMW

instrument,<sup>3,4</sup> operated in the 5-12.5 GHz frequency range, samples were used in the same way as in the CP-FTMW instrument. Ne was used as carrier gas at stagnation pressures ranging up to 3 bar and expanding in pulses of about 800  $\mu$ s through a 0.8 mm nozzle. Short (typ. 0.3  $\mu$ s, 10-300 mW) microwave pulses were used for polarization purposes. Typically, a ca. 400  $\mu$ s-length time domain spectrum was recorded in 40-100 ns intervals and converted to the frequency domain by a fast Fourier transform. Due to the collinear arrangement of the jet and resonator axis each rotational transition splits in two Doppler components so the resonant frequencies are taken as the arithmetic mean of both components. Frequency accuracy is better than 3 kHz.

The analysis<sup>5</sup> of the spectrum was done in two steps. For the first assignments of the A state, we used a semirigid rotor,<sup>6</sup> Hamiltonian in the S-reduction and I<sup>r</sup> representation supplemented with quadrupole coupling<sup>7</sup> terms. For the assignments of the E state, additional perturbation terms<sup>8</sup> to account for the deviations of the E states from the semirigid rotor behaviour, were included. The results of the independent analysis are given in Table S1. In a final step a global fit of the A and E states was done using XIAM program<sup>9</sup> which allows us to determine the rotational, centrifugal distortion, quadrupole coupling constants and internal rotation parameters. In this fit the value of the F reduced rotational constant for the internal rotation was fixed to the value calculated from the CH<sub>3</sub> moment of inertia,  $I_\alpha = 3.20027 \text{ u\AA}^2$ , reported for free acetaldehyde.<sup>10</sup> A summary of the results is given in Table 1 of the paper. The complete results are given in Table S2.

The spectra of <sup>13</sup>C isotopologues observed in their natural abundance were analysed independently for the A and E states by fixing all the parameters to the parent species values with the exception of the rotational constants. The results of the fit are given in Table S3. The complete set of observed frequencies is listed in Tables S11-S19.

The  $r_s$  substitution method of Kraitchman<sup>11</sup> is a purely experimental approach that allows us to locate directly the substituted atoms of a molecule or adduct. It gives the absolute values of the substituted atom coordinates in the principal inertial axis system of the parent molecular system. The signs of the coordinates can be taken from a reasonable molecular structure. Multi-isotopic information can be also used to get the effective ground state  $r_0$  structure. Bond distances and angles are in this case obtained from a least squares fit of all of the available rotational parameters.<sup>12</sup> The results of the application of both  $r_s$  and  $r_0$  methods are summarized in Figure 4. The complete details are given in Tables S7-S9 where they are compared with the ab initio structures for conformer A1 (see Figures 3 and S1).

Full geometry optimizations of plausible forms of the complex PY-AC have been done using ab initio calculations at MP2/aug-cc-pVTZ basis set and CCSD/6-311++G(2d,p) levels.<sup>13</sup> The geometries optimized at this level were used to calculate the corresponding energies using the CCSD(T) method with the same basis set. The initial geometries were considered following the results of the previous work on pyridine formaldehyde (PY-FA).<sup>14</sup> The four conformers found are shown in Figure 3 together with their CCSD(T)/6-311++G(2d,p)//CCSD/6-311++G(2d,p) relative ( $\Delta E$ ) and complexation EBSSE energies, calculated taking into account basis set superposition error (BSSE).<sup>15</sup> The predicted spectroscopic parameters are collected in Tables S4-S5.

The conformers of the adduct were labelled as AI, being I a number indicating the order of CCSD increasing energy. Frequency calculations have confirmed that all the configurations found are true minima. Conformer A1 is stabilized by an  $n \rightarrow \pi^*$  interaction between the imino lone pair and the carbonyl group. A1 is further stabilized by a weak C-H $\cdots$ O contact. From A1, a rotation of formaldehyde around the C=O axis lead to the rupture of the  $n \rightarrow \pi^*$  interaction which is substituted by a weak N $\cdots$ H-C contact in conformer A3. Conformer A2 corresponds to a stack type configuration which could result from dispersion forces or weak

$\pi \rightarrow \sigma^*$  or  $\pi \rightarrow \pi^*$  interactions. Conformer A4, which results from a rotation of acetaldehyde in form A2, shows a weak C-H $\cdots$ N interaction.

Further calculations to test different methods and basis sets were done on the experimentally observed conformer A1. Test were done for B3LYP-D3/6-311++G(2d,p), MP2/6-311++G(2d,p), MP2/6-311++G(3df,2pd), MP2/aug-cc-pVTZ, CCSD/6-311++G(2d,p) or CCSD/aug-cc-pVDZ. The results are shown in Table S6. Globally the best results are obtained for the CCSD methods but CCSD/6-311++G(2d,p) is that which better reproduces the experimental geometrical parameters associated to the non-covalent interactions. This is the reason why this level has been used to report the data of other conformers and in the analysis of the internal rotation of methyl group. B3LYP-D3 gives an acceptable description useful for prediction purposes in bigger systems given the reduced cost of this level compared to other methods.

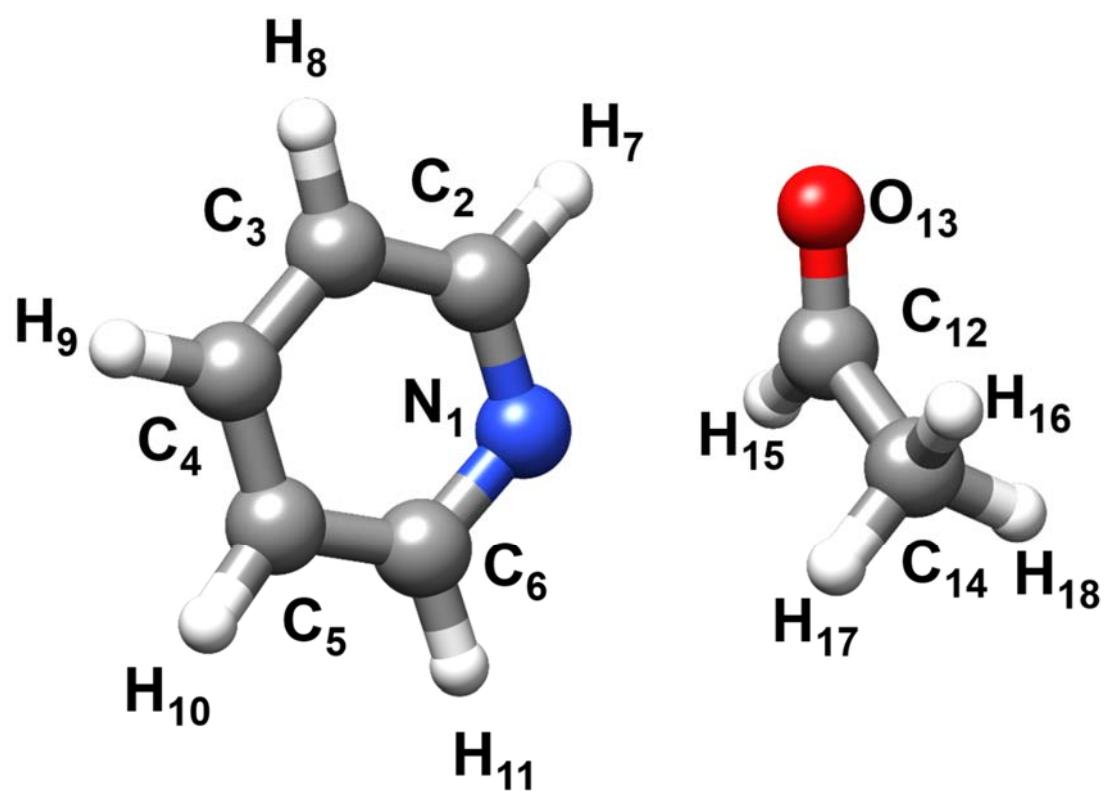
The potential energy surface (PES) of PY-AC is expected to show similar features to that previously investigated for PY-FA<sup>14</sup> to explore the different rotations to interconvert forms A3 into A1, A4 into A2 or the path to interconvert A2 into A1. In this case, small barriers to interconversion were found which explains the collisional conformer relaxation to form A1 in the supersonic jet expansion that precludes the observation of A2-A4 forms.

The interactions responsible for the formation of A1 form have been further investigated using different theoretical methods. A non-covalent interaction (NCI) analysis<sup>16</sup> has been done to visualize the adduct weak interactions. In the NCI plot, intermolecular interactions are visualized as isosurfaces whose color codes indicate the strengths of attractive or repulsive interactions (see Figures 5, S2 and S3). Quantum Theory of “atoms in molecules” (QTAIM)<sup>17,18</sup> has been used to locate bond paths and bond critical points (BCP) in PY-AC (see Figures 5 and S3). Both NCI and QTAIM calculations have been done using Multiwfn<sup>18</sup>

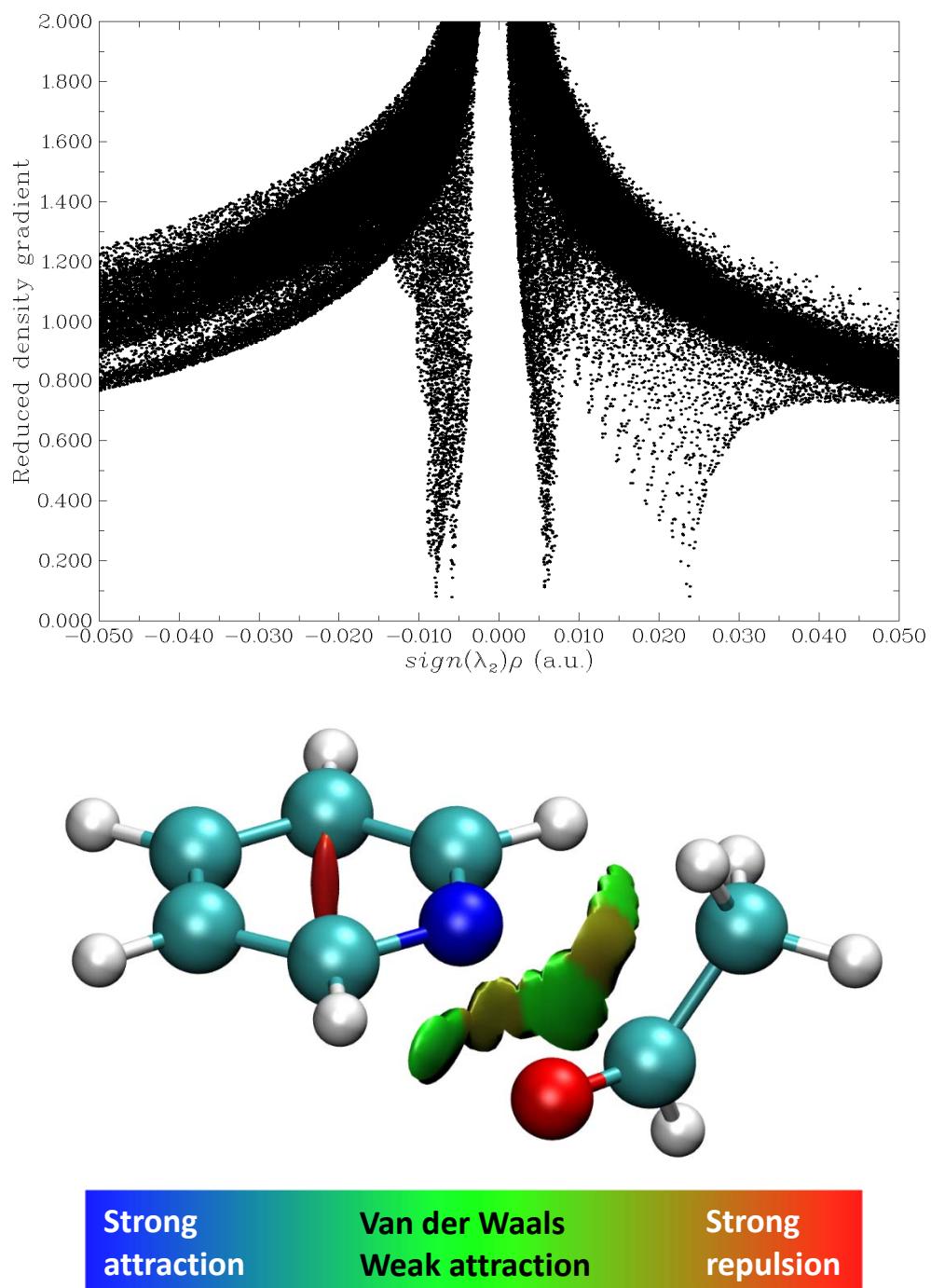
program (see Figures 5, S2 and S3). NBO analysis (see Table S10 and Figure S6) were done using NBO 5.9 package.<sup>19</sup>

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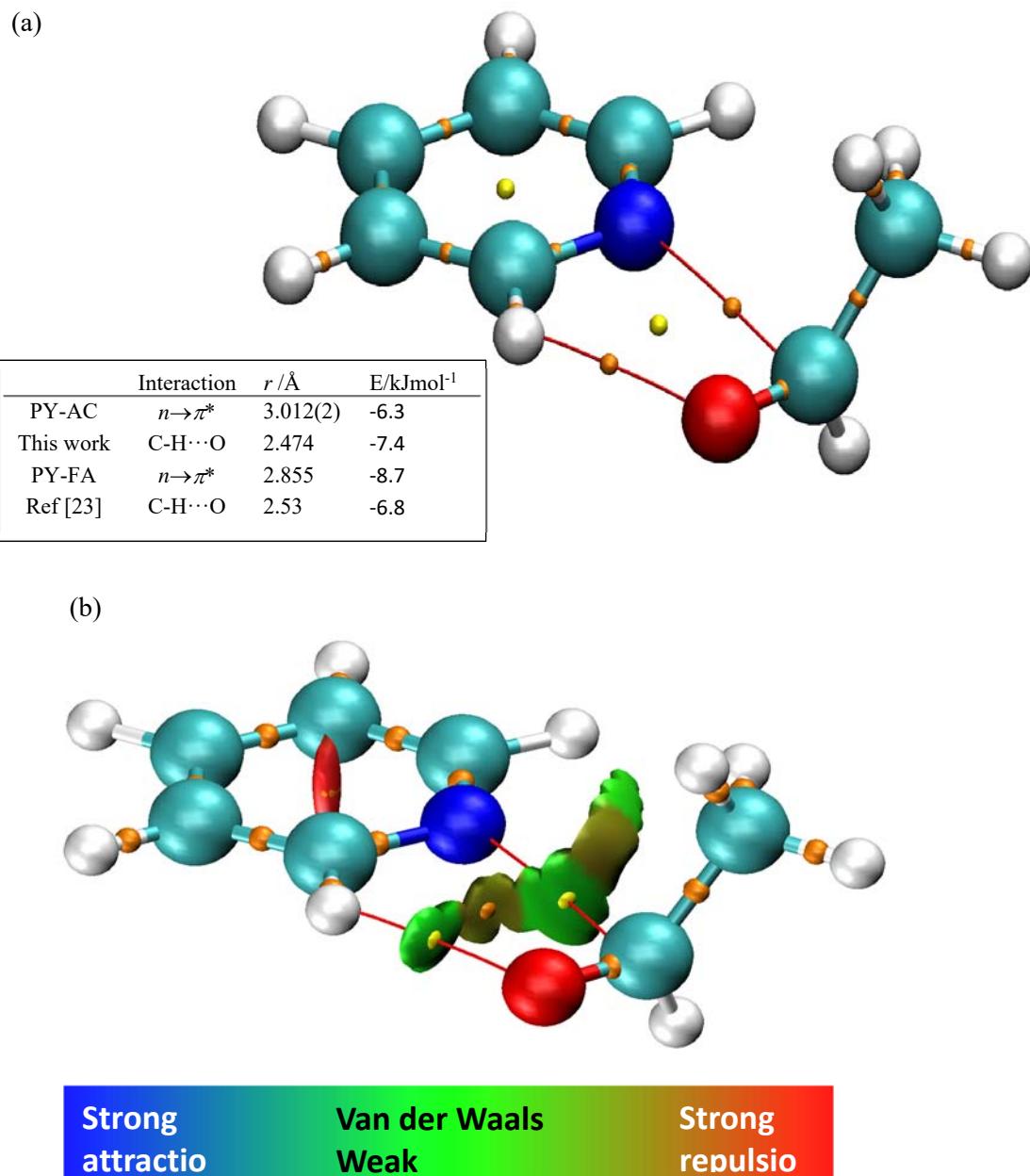
**Figure S1.** Atom labelling for pyridine-acetaldehyde complex conformer A1.



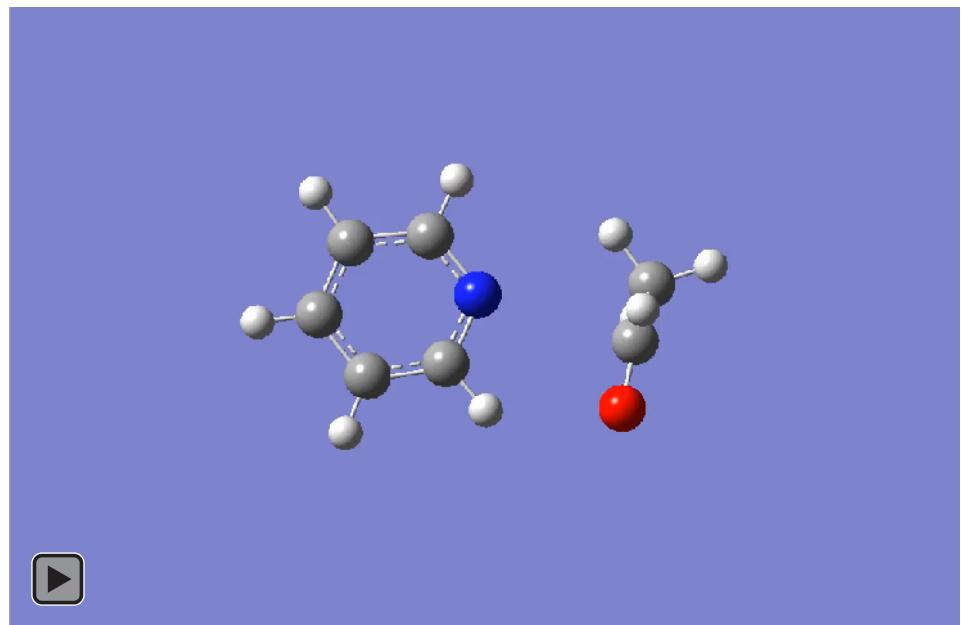
**Figure S2.** Results of the non-covalent interaction (NCI) analysis done using the equilibrium structure  $r_e$  of the pyridine-acetaldehyde complex calculated at CCSD/6-311++G(2d,p) level. Each point in the scatter graph is a grid point in 3D space representing the reduced density gradient (RDG) vs.  $\text{sign}[\lambda_2(\mathbf{r})]\rho(\mathbf{r})$ . The points corresponding to low RDG values correspond to weak interactions. Those with  $\text{RGD} < 0.5 \text{ a.u.}$  are represented in the isosurface below. The spike on the right of the scatter graph correspond to the steric effect region located at the centre of pyridine ring. The other correspond to the van der Waals interaction region located between both molecules (E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 6498–6506).



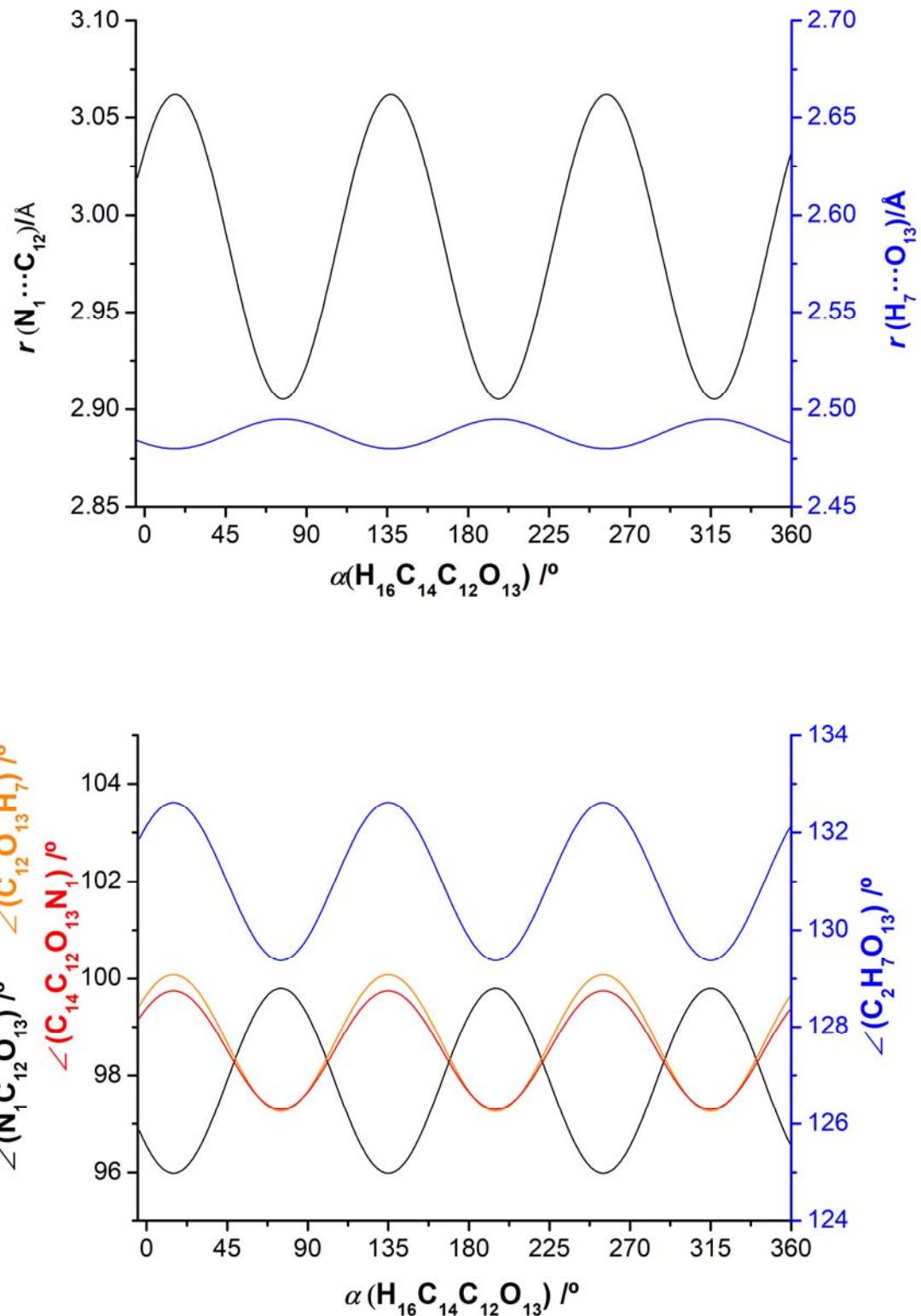
**Figure S3.** Results of Quantum Theory of “atoms in molecules” (QTAIM) applied to locate bond paths (BP) and bond critical points (BCP) in PY-AC. The results are summarized in (a) where BP are in red, and ring and bond BCPs are given in yellow and orange respectively. The BPs and BCPs for both the  $n \rightarrow \pi^*$  and the weak C-H $\cdots$ O interactions are shown. The equilibrium structure  $r_e$  of the pyridine-acetaldehyde complex calculated at CCSD/6-311++G(2d,p) level has been considered. The strength of the non-covalent interactions estimated from the electron potential density  $V(r)$  at the BCPs are compared in the table to those of PY-formaldehyde (PY-FA) complex. (b) The combination of QTAIM result and the NCI isosurface allows us to correlate the bond critical points with the van der Waals interaction regions.



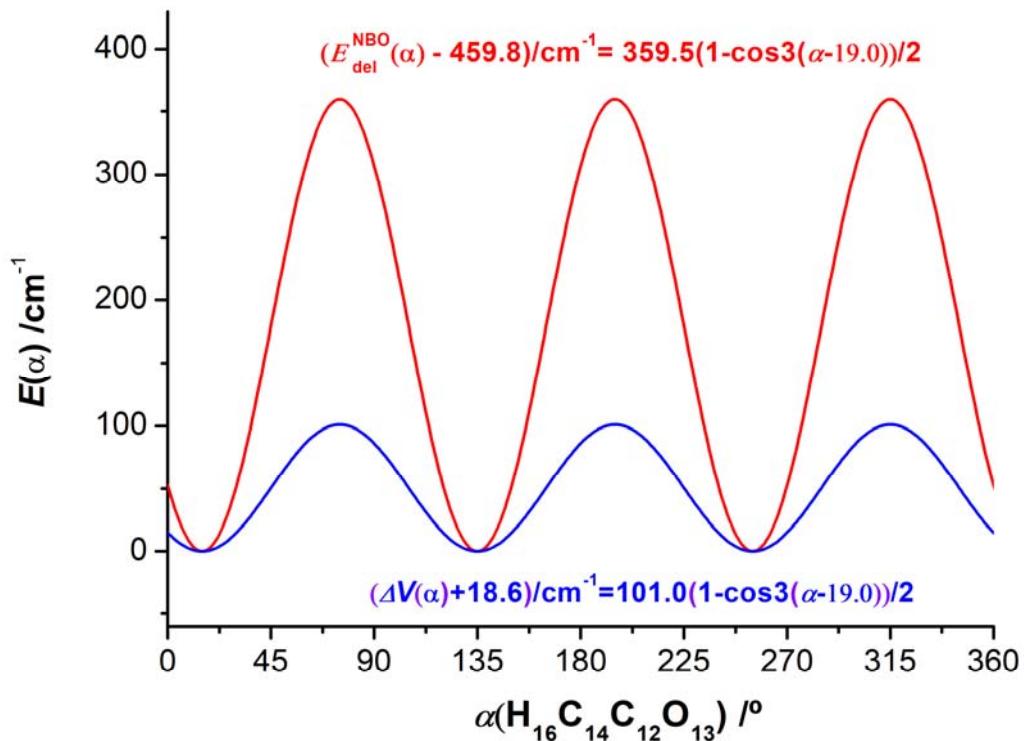
**Figure S4.** Animated figure illustrating the large amplitude oscillations geared to the internal rotation of the methyl group in pyridine-acetaldehyde complex. These oscillations affect mainly to the  $n\rightarrow\pi^*$  interaction distance  $r(N_1\cdots C_{12})$ .



**Figure S5.** Figure illustrating the variation of the intermolecular  $r(N_1 \cdots C_{12})$  and  $r(H_7 \cdots O_{13})$  distances (in Å) (upper plot), the intermolecular angles  $\angle N_1 C_{12} O_{13}$ ,  $\angle C_{12} O_{13} H_7$ ,  $\angle C_2 H_7 O_{13}$  or the dihedral angle  $\angle C_{14} C_{12} O_{13} N_1$  (in degree) (lower plot) with the methyl top internal coordinate  $\alpha$ . In all cases, the variation can be fitted to an expression:  $P(\alpha) = P_0 + P_3(1 - \cos 3(\alpha - \tau))/2$ .  $P_0$  and  $P_3$  takes values of (3.062, -0.156), (2.480, 0.013), (95.98, 3.8), (100.1, -2.8), (132.6, -3.2) and (99.7, -2.3) for  $r(N_1 C_{12})$ ,  $r(H_7 O_{13})$ ,  $\angle N_1 C_{12} O_{13}$ ,  $\angle C_{12} O_{13} H_7$ ,  $\angle C_2 H_7 O_{13}$  and  $\angle C_{14} C_{12} O_{13} N_1$ , respectively. In all cases the phase angle is  $\tau = 19^\circ$ .



**Figure S6.** Figure comparing the function  $\Delta V(\alpha)$  (see Figure 6) and the  $E_{\text{del}}(\alpha)$  predicted NBO donor→acceptor  $n \rightarrow \pi^*$  stabilization energy calculated by deletion-type reoptimization (See Table S10).  $\Delta V(\alpha)$  is a pseudo-experimental function obtained from the difference between the experimental methyl group internal rotation potential energies for the free and complexed acetaldehyde, but considering that the equilibrium values for the latter are displaced  $-4^\circ$  with respect to free acetaldehyde as predicted by CCSD/6-311++G(2d,p) calculations. Both functions fit to an expression:  $V(\alpha) = V_0 + V_3(1 - \cos 3(\alpha - \tau))/2$ . Both pseudo-experimental and calculated NBO functions have the same phase angle,  $\tau = -19^\circ$  but the  $V_3$  value measuring the  $n \rightarrow \pi^*$  interaction energy in the interval with values of  $r(N_1C_{12})$  between 3.062 and 2.906 Å, seems to be overestimated by the NBO type calculations.



**Table S1.** Rotational parameters obtained from the separate semirigid rotor analysis of the A and E methyl torsion states of the pyridine-acetaldehyde adduct and their comparison with the CCSD/6311++G(2d,p) *ab initio* constants for the most stable form A1 of the complex (see Figure 1 and Tables S4-S6)

Fitted Parameters <sup>a</sup>	A	E	<i>Ab initio</i> A1
<i>A</i> /MHz	3633.73192(56) <sup>b</sup>	3633.7122(10)	3646.31
<i>B</i> /MHz	778.44089(13)	778.42534(22)	775.08
<i>C</i> /MHz	667.93203(11)	667.91663(17)	662.00
<i>D<sub>J</sub></i> /kHz	0.3629(10)	0.3642(12)	
<i>D<sub>JK</sub></i> /kHz	1.1018(68)	1.1008(87)	
<i>D<sub>K</sub></i> /kHz	[0.]	[0.]	
<i>d<sub>1</sub></i> /kHz	-0.02757(91)	-0.0391(13))	
<i>d<sub>2</sub></i> /kHz	-0.00993(41)	-0.00939(56)	
<i>D<sub>a</sub></i> /MHz	-	-2.9345(43)	
<i>D<sub>aJ</sub></i> /MHz		-0.01020(88)	
<i>D<sub>c</sub></i> /MHz	-	2.840(48)	
1.5( $\chi_{aa}$ )/MHz	-6.0240(34)	-6.0244(43)	-6.50
0.25( $\chi_{bb}-\chi_{cc}$ ) /MHz	-0.56445(95)	-0.5648(12)	-0.61
n	194	179	
$\sigma$ /kHz	7.3	7.1	
Derived Parameters			
<i>P<sub>a</sub></i> /uÅ <sup>2</sup>	633.38608(13)	633.40095(21)	638.43
<i>P<sub>b</sub></i> /uÅ <sup>2</sup>	123.24644(13)	123.24902(21)	124.99
<i>P<sub>c</sub></i> /uÅ <sup>2</sup>	15.83346(13)	15.83164(21)	13.61
$\chi_{aa}$ /MHz	-4.0160(23)	-4.0163(29)	-4.33
$\chi_{bb}$ /MHz	0.8791(30)	0.8785(38)	0.96
$\chi_{cc}$ /MHz	3.1369(30)	3.1377(38)	3.38

<sup>a</sup> *A*, *B* and *C* are rotational constants. *D<sub>J</sub>*, *D<sub>JK</sub>*, *D<sub>K</sub>*, *d<sub>1</sub>*, *d<sub>2</sub>* are quartic centrifugal distortion constants. *D<sub>a</sub>*, *D<sub>b</sub>* and *D<sub>c</sub>* are the coefficients of angular momentum perturbation operators: *D<sub>a</sub>P<sub>a</sub>+D<sub>b</sub>P<sub>b</sub>+D<sub>c</sub>P<sub>c</sub>* needed to account for the deviations of the E rotational transitions from the semirigid rotor behavior. In the present case only *D<sub>a</sub>* and *D<sub>c</sub>* are determinable. *D<sub>aJ</sub>* is a centrifugal distortion term associated to *D<sub>a</sub>*.  $\chi_{aa}$ ,  $\chi_{bb}$  and  $\chi_{cc}$  are <sup>14</sup>N nuclear quadrupole coupling constants. n is the number of hyperfine quadrupole components fitted.  $\sigma$  is the rms deviation of the fit. *P<sub>α</sub>* ( $\alpha=a$ ,  $b$  or  $c$ ) are planar moments of inertia derived from the moments of inertia *I<sub>α</sub>* as for example  $P_c=(I_a+I_b-I_c)/2$ . <sup>b</sup> Standard errors are given in parentheses in units of the last digit.

**Table S2.** Rotational parameters obtained from the internal rotation analysis of the pyridine-acetaldehyde spectrum.

Fitted Parameters <sup>a</sup>		Fixed Parameters	
<i>A</i> /MHz	3633.72143(76) <sup>b</sup>	<i>I</i> <sub>a</sub> /uÅ <sup>2</sup>	[3.20027] <sup>c</sup>
<i>B</i> /MHz	778.43114(12)	<i>F</i> <sub>0</sub> /GHz	[157.9176] <sup>c</sup>
<i>C</i> /MHz	667.92408(11)	<i>F</i> /GHz	[158.7367] <sup>c</sup>
<i>D</i> <sub>J</sub> /kHz	0.36292(82)		
<i>D</i> <sub>JK</sub> /kHz	1.09899(57)	Derived Parameters	
<i>D</i> <sub>K</sub> /kHz	1.50(26)	∠( <i>i,a</i> ) <sup>o</sup>	79.804(43)
<i>d</i> <sub>1</sub> /kHz	-0.03025(78)	∠( <i>i,b</i> ) <sup>o</sup>	134.37(13)
<i>d</i> <sub>2</sub> /kHz	-0.00881(38)	∠( <i>i,c</i> ) <sup>o</sup>	46.16(12)
$\chi_{aa}$ /MHz	-4.0159(19)	<i>s</i>	28.842(27)
( $\chi_{bb}$ - $\chi_{cc}$ ) /MHz	-2.2587(32)		
<i>V</i> <sub>3</sub> /GHz	10301.0(95)	<i>P</i> <sub>a</sub> /uÅ <sup>2</sup>	633.39449(13)
<i>V</i> <sub>3</sub> /cm <sup>-1</sup>	343.60(32)	<i>P</i> <sub>b</sub> /uÅ <sup>2</sup>	123.24704(13)
<i>V</i> <sub>3</sub> /kJmol <sup>-1</sup>	0.98173(90)	<i>P</i> <sub>c</sub> /uÅ <sup>2</sup>	15.83326(13)
<i>D</i> <sub>piJ</sub> /kHz	-54.5(16)	$\chi_{aa}$ /MHz	-4.0159(19)
$\varepsilon$ /rad	2.3610(21)	$\chi_{bb}$ /MHz	0.8756(26)
$\delta$ /rad	1.39284(76)	$\chi_{cc}$ /MHz	3.1373(26)
n	373		
$\sigma$ /kHz	3.5		

<sup>a</sup> *A*, *B* and *C* are rotational constants. *D*<sub>J</sub>, *D*<sub>JK</sub>, *D*<sub>K</sub>, *d*<sub>1</sub>, *d*<sub>2</sub> are quartic centrifugal distortion constants.  $\chi_{aa}$ ,  $\chi_{bb}$  and  $\chi_{cc}$  are <sup>14</sup>N nuclear quadrupole coupling constants. *V*<sub>3</sub> is the internal rotation barrier. *D*<sub>piJ</sub> is an empirical internal rotation-overall rotation distortion parameter [N.Hansen, H.Mader and T.Bruhn, *Molec. Phys.* **1999**, 97, 587-595].  $\delta$  is the angle of the internal rotation axis with the *a* inertial axis.  $\varepsilon$  is the angle between the principal inertial axis *b* and the projection of the internal rotation axis onto the *bc* plane. n is the number of hyperfine quadrupole components fitted.  $\sigma$  is the standard deviation of the fit. *I*<sub>a</sub> is the moment of inertia of methyl top. *F*<sub>0</sub> is the methyl top internal rotational constant:  $F_0 = h/(8\pi^2 r I_a)$ . *F* is the methyl top internal rotational reduced constant  $F = F/r$  ( $r = 1 - \sum_g (\lambda_g^2 I_a/I_g)$ ;  $g = a, b, c$ ;  $\lambda_g = \cos(\angle(i,g))$ ).  $\angle(i,a)$ ,  $\angle(i,b)$ ,  $\angle(i,c)$  are the angles between the methyl top axis and the inertial axes *a*, *b* and *c* ( $\delta = \angle(i,a)$ ) ; *s* is the reduced barrier,  $s = 4V_3/9F$ . *P* <sub>$\alpha$</sub>  ( $\alpha = a, b$  or *c*) are planar moments of inertia derived from the moments of inertia as for example  $P_c = (I_a + I_b - I_c)/2$ .

<sup>b</sup> Standard errors are given in parentheses in units of the last digit.

<sup>c</sup> Parameters in square brackets were kept fixed. *I*<sub>a</sub> was assumed to have the same value as in acetaldehyde [H. Maes, G. Włodarczak, D. Doucher and J. Demaison. *Z. Naturforsch.*, **1987**, 42a, 97-102].

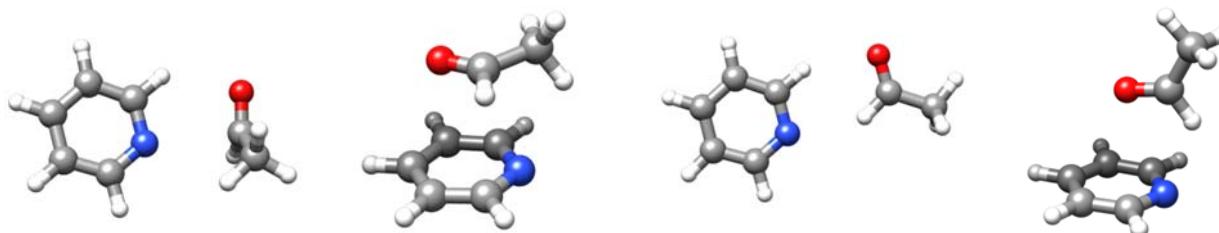
**Table S3.** Rotational constants obtained from the analysis of the spectra of the observed  $^{13}\text{C}$  isotopologues of the pyridine-acetaldehyde cluster,

Parameters <sup>a</sup>	$\text{C}_2$		$\text{C}_3$	
	A	E	A	E
$A/\text{MHz}$	3614.884(39)	3615.089(46)	3587.991(68)	3588.249(71)
$B/\text{MHz}$	778.120580(80)	778.104760(96)	774.33245(21)	774.31606(23)
$C/\text{MHz}$	667.064640(80)	667.049230(93)	663.44579(14)	663.43068(19)
$P_c/\text{u}\text{\AA}^2$	15.83778(83)	15.83166(98)	15.8841(15)	15.8773(16)
n	18	18	15	15
$\sigma/\text{kHz}$	1.0	1.2	1.6	3.0
$\text{C}_4$				
	A	E	A	E
$A^a/\text{MHz}$	3628.7750(12)	3628.7573(15)	3611.718 (72)	3611.820(62)
$B/\text{MHz}$	768.48690(18)	768.47171(19)	770.38051(21)	770.36466(18)
$C/\text{MHz}$	660.47748(12)	660.46242(13)	661.26151(14)	661.24661(12)
$P_c/\text{u}\text{\AA}^2$	15.86316(17)	15.86128(19)	15.8374(16)	15.8336(14)
n	18	17	15	15
$\sigma/\text{kHz}$	1.6	1.7	1.7	1.4
$\text{C}_6$				
	A	E	A	E
$A^a/\text{MHz}$	3589.043 (83)	3589.299(75)	3629.621(45)	3629.900(55)
$B/\text{MHz}$	776.44755(25)	776.43181(23)	769.54100(12)	769.52591(15)
$C/\text{MHz}$	665.05757(17)	665.04173(15)	661.501210(87)	661.48549(10)
$P_c/\text{u}\text{\AA}^2$	15.8976(18)	15.8901(17)	15.98861(96)	15.9806(12)
n	15	15	15	15
$\sigma/\text{kHz}$	2.0	1.8	1.0	1.2
$\text{C}_{14}$				
	A	E		
$A^a/\text{MHz}$	3594.8670 (16)	3594.8389(55)		
$B/\text{MHz}$	767.37355(15)	767.35797(61)		
$C/\text{MHz}$	659.14422(10)	659.12968(38)		
$P_c/\text{u}\text{\AA}^2$	16.22318(15)	16.22196(19)		
n	16	16		
$\sigma/\text{kHz}$	1.3	1.6		

<sup>a</sup> A, B and C are rotational constants.  $P_c = (I_a + I_b - I_c)/2$ . . n is the number of hyperfine quadrupole components fitted.  $\sigma$  is the standard deviation of the fit.

**Table S4.** Spectroscopic parameters and energies calculated for the lowest energy forms found for the pyridine-acetaldehyde adduct at MP2/aug-cc-pVTZ level.

Parameters <sup>a</sup>	A1	A2	A3	A4
A/MHz	3610.16	2408.05	4225.31	2893.81
B/MHz	830.23	1262.29	617.42	890.63
C/MHz	709.73	1174.24	540.49	883.04
P <sub>a</sub> /μÅ <sup>2</sup>	590.40	310.44	816.98	482.56
P <sub>b</sub> /μÅ <sup>2</sup>	121.67	119.95	118.06	89.76
P <sub>c</sub> /μÅ <sup>2</sup>	18.32	89.92	1.55	84.88
1.5χ <sub>aa</sub> /MHz	-6.06	2.66	-6.67	5.11
0.25(χ <sub>bb</sub> -χ <sub>cc</sub> )/MHz	-0.56	-1.05	-0.61	-1.50
χ <sub>ab</sub> /MHz	1.46	-3.22	-1.24	0.03
χ <sub>ac</sub> /MHz	1.24	-0.15	0.00	0.00
χ <sub>bc</sub> /MHz	-0.64	-0.81	0.00	0.00
μ <sub>a</sub> /D	-2.44	0.14	0.14	0.91
μ <sub>b</sub> /D	-2.03	0.03	2.17	-0.08
μ <sub>c</sub> /D	0.42	-0.55	0.00	0.00
E/h	-401.340918	-401.341029	-401.338911	-401.337646
ΔE/kJmol <sup>-1</sup>	0.29	0.00	5.56	8.88
D <sub>E</sub> (BSSE)	20.5	19.5	5.9	12.0



<sup>a</sup> A, B and C are the rotational constants. P<sub>a</sub> ( $\alpha = a, b$  or  $c$ ) are the planar moments of inertia derived from the moments of inertia I<sub>a</sub> as for example  $P_c = (I_a + I_b - I_c)/2$ . χ<sub>aa</sub>, χ<sub>bb</sub>, χ<sub>cc</sub>, are the <sup>14</sup>N quadrupole coupling constants. μ<sub>a</sub>, μ<sub>b</sub> and μ<sub>c</sub> 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 and D<sub>E</sub>(BSSE) dissociation energy calculated using counterpoise procedure (S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566).

**Table S5.** Spectroscopic parameters and energies calculated for the lowest energy forms found for the pyridine-acetaldehyde adduct at CCSD/6-311++G(2d,p) level. The energies calculated at CCSD(T)/ 6-311++G(2d,p) level for the CCSD geometries are given.

Parameters <sup>a</sup>	A1	A2	A3	A4
A/MHz	3646.31	2372.09	4256.37	2899.00
B/MHz	775.08	1145.22	597.37	820.01
C/MHz	662.00	1065.88	525.55	814.28
P <sub>a</sub> /μÅ <sup>2</sup>	638.43	351.19	844.45	531.31
P <sub>b</sub> /μÅ <sup>2</sup>	124.99	122.95	117.17	89.33
P <sub>c</sub> /μÅ <sup>2</sup>	13.61	90.10	1.57	85.00
1.5χ <sub>aa</sub> /MHz	-6.50	2.74	-6.98	5.27
0.25(χ <sub>bb</sub> -χ <sub>cc</sub> )/MHz	-0.61	-1.20	-0.61	-1.64
χ <sub>ab</sub> /MHz	-1.83	-3.40	-1.55	-0.01
χ <sub>ac</sub> /MHz	0.87	-0.06	0.00	0.00
χ <sub>bc</sub> /MHz	0.52	-0.64	0.00	0.00
μ <sub>a</sub> /D	-2.37	0.16	0.00	0.65
μ <sub>b</sub> /D	2.01	-0.15	2.14	-0.22
μ <sub>c</sub> /D	0.04	-0.56	0.00	0.00
E/h	-401.1881153	-401.1866411	-401.1870528	-401.1847726
ΔE/kJmol <sup>-1</sup>	0.0	3.9	2.8	8.8
D <sub>E</sub> (BSSE)/ kJmol <sup>-1</sup>	14.4	9.6	12.6	5.7
E <sub>CCSD(T)</sub> /h	-401.259068	-401.257948	-401.257776	-401.255754
ΔE <sub>CCSD(T)</sub> /kJmol <sup>-1</sup>	0.0	3.9	2.4	8.5
D <sub>E</sub> (BSSE) <sub>CCSD(T)</sub> /kJmol <sup>-1</sup>	15.9	12.0	13.6	7.4



<sup>a</sup> A, B and C are the rotational constants. P<sub>α</sub> ( $\alpha = a, b$  or  $c$ ) are the planar moments of inertia derived from the moments of inertia I<sub>α</sub> as for example  $P_a = (I_a + I_b - I_c)/2$ . χ<sub>aa</sub>, χ<sub>bb</sub>, χ<sub>cc</sub>, are the <sup>14</sup>N quadrupole coupling constants. μ<sub>a</sub>, μ<sub>b</sub> and μ<sub>c</sub> 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 and D<sub>E</sub>(BSSE) dissociation energy calculated using counterpoise procedure (S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566).

**Table S6.** Spectroscopic parameters calculated for the low energy form A1 of the pyridine-acetaldehyde adduct at different levels of theory. The best description correspond to CCSD/6-311++G(2d,p) level (see Figure 3 and S1).

Parameters <sup>a</sup>	B3LYP-D3/6-311++G(d,p)	MP2/6-311++G(2d,p)	MP2/6-311++G(3df,2dp)	MP2/aug-CC-pVTZ	CCSD/6-311++G(2d,p)	CCSD/aug-CC-pVDZ	exp
A/MHz	3633.10	3620.00971	3599.36	3610.2	3646.31	3578.48	3633.7214(8)
B/MHz	802.90	812.63716	832.25	830.2	775.08	787.84	778.4311(1)
C/MHz	685.76	691.44352	711.56	709.7	662.00	671.99	667.9241(1)
P <sub>a</sub> /μÅ <sup>2</sup>	613.65	606.60	588.54	590.40	638.43	626.15	633.3945(1)
P <sub>b</sub> /μÅ <sup>2</sup>	123.31	124.31	121.70	121.67	124.99	125.91	123.2470(1)
P <sub>c</sub> /μÅ <sup>2</sup>	15.79	15.30	18.71	18.32	13.61	15.32	15.8333(1)
1.5χ <sub>aa</sub> /MHz	-6.69	-6.24	-6.15	-6.06	-6.50	-5.89	-6.024(3)
0.25(χ <sub>bb</sub> -χ <sub>cc</sub> )/MHz	-0.54	-0.57	-0.55	-0.56	-0.61	-0.49	-0.564(1)
V <sub>3</sub> (PY-AC)/cm <sup>-1</sup>	333.1	346.0	348.2	356.7	344.4	329.2	343.6(3)
α <sub>e</sub> (PY-AC)/°	-4.37	-8.1	-8.6	-7.1	-4.0	-3.9	-
V <sub>3</sub> (AC)/cm <sup>-1</sup>	383.1	395.4	403.5	413.9	386.1	404.3	407.59768 <sup>b</sup>
ΔV <sub>3</sub> /cm <sup>-1</sup>	-50.0	-49.5	-55.4	-57.2	-41.7	-75.2	-64.0
r(C <sub>12</sub> N <sub>1</sub> )/Å	2.915	2.889	2.889	2.846	3.012	2.953	3.012(2)
r(O <sub>13</sub> H <sub>7</sub> )/Å	2.427	2.395	2.395	2.349	2.478	2.438	2.474(3)
∠N <sub>1</sub> C <sub>12</sub> O <sub>13</sub> /°	96.6	96.40	96.0	96.25	96.7	97.0	96.9(2)
∠C <sub>12</sub> O <sub>13</sub> H <sub>7</sub> /°	100.7	100.95	101.6	101.3	99.7	100.0	99.8(1)
∠C <sub>14</sub> C <sub>12</sub> O <sub>13</sub> N <sub>1</sub> /°	-99.3	-98.1	-96.8	-97.4	-99.6	-98.9	-97.7(2)
∠(i,a)/°	78.1	78.9	81.9	80.9	76.8	78.4	79.80(4)
∠(i,b)/°	133.8	134.7	132.0	131.6	136.2	134.9	134.4(1)
∠(i,c)/°	46.2	46.8	43.1	43.0	49.2	47.2	46.2(1)

<sup>a</sup> A, B and C are the rotational constants. P<sub>α</sub> ( $\alpha = a, b$  or  $c$ ) are the planar moments of inertia derived from the moments of inertia I<sub>α</sub> as for example  $P_c = (I_a + I_b - I_c)/2$ . χ<sub>aa</sub>, χ<sub>bb</sub>, χ<sub>cc</sub>, are the <sup>14</sup>N quadrupole coupling constants. V<sub>3</sub> is the barrier to internal rotation of the methyl group. α<sub>e</sub> is the equilibrium internal rotation angle, α<sub>e</sub>=∠H<sub>16</sub>-C<sub>14</sub>-C<sub>12</sub>-O<sub>13</sub>. ∠(i,a), ∠(i,b), ∠(i,c) are the angles between the methyl top axis and the inertial axes *a*, *b* and *c*. <sup>b</sup> Taken from reference 24.

**Table S7.**  $r_s$  coordinates (in Å) of the isotopically substituted atoms of the complex pyridine-acetaldehyde, compared to the  $r_0$  and  $r_e$  coordinates calculated at MP2/aug-cc-pVTZ ( $r_{e1}$ ) and CCSD/6-311++G(2d,p) ( $r_{e2}$ ) levels. See Figures 1 and S1 for atom labelling.

		<i>a</i>	<i>b</i>	<i>c</i>
$ r_s ^a$	$C_2$	0.5137(30) <sup>b</sup>	0.8513(18)	0.066(23)
$r_0$		-0.55024(92) <sup>c</sup>	0.8490(11)	0.0492(11)
$r_{e1}$		-0.5053	0.8786	0.0206
$r_{e2}$		-0.5669	0.8596	0.0460
$ r_s $	$C_3$	1.84349(89)	1.3196(13)	0.2281(72)
$r_0$		-1.8503(14)	1.32247(34)	0.24009(20)
$r_{e1}$		-1.8070	1.3112	0.2630
$r_{e2}$		-1.8737	1.3172	0.2136
$ r_s $	$C_4$	2.90113(52)	0.4045(37)	0.1741(86)
$r_0$		-2.90539(46)	0.4141(14)	0.17353(51)
$r_{e1}$		-2.8436	0.3845	0.2166
$r_{e2}$		-2.9165	0.3974	0.1548
$ r_s $	$C_5$	2.60959(63)	0.9269(18)	0.064(26)
$r_0$		-2.61481(96)	-0.9253(11)	-0.08053(88)
$r_{e1}$		-2.5330	-0.9408	-0.0719
$r_{e2}$		-2.6088	-0.9424	-0.0695
$ r_s $	$C_6$	1.2668(14)	1.2961(13)	0.2562(67)
$r_0$		-1.2797(14)	-1.29576(37)	-0.25676(27)
$r_{e1}$		-1.2022	-1.2801	-0.3002
$r_{e2}$		-1.2707	-1.2991	-0.2237
$ r_s $	$C_{12}$	2.71581(65)	0.105(17)	0.4111(43)
$r_0$		2.7228(16)	-0.02524(32)	-0.29000(44)
$r_{e1}$		2.6283	-0.0565	-0.3860
$r_{e2}$		2.7216	-0.0006	-0.4083
$ r_s $	$C_{14}$	2.99853(50)	1.0653(14)	0.6336(24)
$r_0$		3.0012(15)	-1.07361(35)	0.63779(11)
$r_{e1}$		2.8654	-1.0504	0.7085
$r_{e2}$		3.0582	-1.0871	0.5757

<sup>a</sup> Absolute values. <sup>b</sup>Errors quoted in parenthesis in units of the last digit for  $r_s$  values calculated according to C. C. Costain, *Trans. Am. Crystallogr. Assoc.* **1966**, *2*, 157-164. <sup>c</sup> Estimated standard errors quoted in parenthesis in units of the last digit for  $r_0$  values.

**Table S8.**  $r_0$  structure of pyridine-acetaldehyde compared to the  $r_e$  MP2/aug-cc-pVTZ ( $r_{e1}$ ), CCSD/6-311++G(2d,p) ( $r_{e2}$ ) and  $r_s$  structures. See Figures 3 and S1 for atom labelling.

	$r_0$	$r_{e1}$	$r_{e2}$	$r_s$
pyridine <sup>a</sup>				
$r(N_1-C_2)/\text{\AA}$	[1.3403]	1.34144	1.33941	
$r(C_2-C_3)/\text{\AA}$	[1.3967]	1.39288	1.39481	1.4191 (41) <sup>c</sup>
$r(C_3-C_4)/\text{\AA}$	[1.3939]	1.39123	1.39171	1.3995(27)
$r(C_4-C_5)/\text{\AA}$	[1.3939]	1.39139	1.39289	1.3835 (62)
$r(C_5-C_6)/\text{\AA}$	[1.3967]	1.39228	1.39333	1.4058 (40)
$r(N_1-C_6)/\text{\AA}$	[1.3403]	1.34141	1.33926	
$r(C_2-H_7)/\text{\AA}$	[1.0844]	1.08392	1.08640	
$r(C_3-H_8)/\text{\AA}$	[1.0807]	1.08147	1.08480	
$r(C_4-H_9)/\text{\AA}$	[1.0812]	1.08195	1.08572	
$r(C_5-H_{10})/\text{\AA}$	[1.0807]	1.08148	1.08487	
$r(C_6-H_{11})/\text{\AA}$	[1.0844]	1.08408	1.08738	
$\angle N_1-C_2-C_3/^\circ$	[123.74]	123.23637	123.42291	
$\angle C_2-C_3-C_4/^\circ$	[118.50]	118.92277	118.69680	119.21(21)
$\angle C_3-C_4-C_5/^\circ$	[118.50]	118.36240	118.48925	118.46(15)
$\angle C_4-C_5-C_6/^\circ$	[118.50]	118.65092	118.43787	118.53(14)
$\angle C_5-C_6-N_1/^\circ$	[123.74]	123.54681	123.74179	
$\angle C_6-N_1-C_2/^\circ$	[117.03]	117.28068	117.21131	
$\angle H_7-C_2-N_1/^\circ$	[116.12]	115.63860	115.88154	
$\angle H_8-C_3-C_2/^\circ$	[120.00]	119.89679	119.96939	
$\angle H_9-C_4-C_3/^\circ$	[120.75]	120.84991	120.78442	
$\angle H_{10}-C_5-C_6/^\circ$	[120.00]	120.06470	120.16866	
$\angle H_{11}-C_6-N_1/^\circ$	[116.12]	116.07803	116.07941	
$\angle C_2-C_3-C_4-C_5/^\circ$	[0.0]	-0.02332	-0.01695	-1.3(1.9)
$\angle C_3-C_4-C_5-C_6/^\circ$	[0.0]	0.02636	0.07740	-0.8(2.5)
acetaldehyde <sup>b</sup>				
$r(C_{12}-O_{13})/\text{\AA}$	[1.2038]	1.21812	1.20982	
$r(C_{12}-C_{14})/\text{\AA}$	[1.5005]	1.49729	1.50552	1.447(12)
$r(C_{12}-H_{15})/\text{\AA}$	[1.1237]	1.10240	1.10631	
$r(C_{14}-H_{16})/\text{\AA}$	[1.090]	1.08663	1.09097	
$r(C_{14}-H_{17})/\text{\AA}$	[1.090]	1.08879	1.09321	
$r(C_{14}-H_{18})/\text{\AA}$	[1.090]	1.09213	1.09594	
$\angle C_{14}-C_{12}-O_{13}/^\circ$	[124.72]	124.16362	124.22378	
$\angle H_{15}-C_{12}-O_{13}/^\circ$	[113.93]	115.63815	120.14558	
$\angle H_{16}-C_{14}-C_{12}/^\circ$	[109.3]	110.54679	110.46755	
$\angle H_{17}-C_{14}-C_{12}/^\circ$	[109.3]	109.18590	109.08435	
$\angle H_{18}-C_{14}-C_{12}/^\circ$	[109.3]	108.86135	109.19047	
$\angle H_{15}-C_{12}-O_{13}-C_{14}/^\circ$	[-180.00]	-177.83142	-178.89046	
$\angle H_{16}-C_{14}-C_{12}-O_{13}/^\circ$	[0.00]	7.32175	3.95504	
$\angle H_{17}-C_{14}-C_{12}-H_{16}/^\circ$	[120.88]	121.79617	121.46508	
$\angle H_{18}-C_{14}-C_{12}-H_{16}/^\circ$	[-120.88]	-120.67430	-120.84158	

<sup>a</sup> The structural parameters of pyridine given in square brackets were fixed to the values reported in ref [22]. <sup>b</sup> The structural parameters of acetaldehyde given in square brackets were fixed to the values previously reported [A. Bauder, F. J. Lovas, and D. R. Johnson, *J. Phys. Chem. Ref. Data*, **1976**, *5*, 53-77], except for methyl group which was fixed to a local  $C_3$  symmetry to give a value of  $I_a=3.20 \text{ u\AA}^2$ . <sup>c</sup> Standard errors in parenthesis in units of the last digit. <sup>d</sup> Derived values.

**Table S8.** (continued)

	$r_0$	$r_{e1}$	$r_{e2}$	$r_s$	$r_0$
PY-acetaldehyde					PY-CH <sub>2</sub> O
$r(N_1-C_{12})/\text{\AA}$	3.0119(17) <sup>c</sup>	2.84557	3.01191		2.8554(42)
$\angle C_4-N_1-C_{12}/^\circ$	154.272(80)	155.79083	154.70556		156.51(86)
$\angle N_1-C_{12}-O_{13}/^\circ$	96.88(17)	96.23922	96.72615		102.79(58)
$\angle C_{12}-N_1-C_4-C_3/^\circ$	-0.94(18)	7.50693	-3.43995		0.
$\angle C_2-N_1-C_{12}-O_{13}/^\circ$	0.284(27)	-3.75330	4.45933		0.
$\angle C_{14}-C_{12}-O_{13}-N_1/^\circ$	-97.74(18)	-97.38755	-99.60666		
$r(O_{13}-H_7)/\text{\AA}$	2.4742(27) <sup>d</sup>	2.34860	2.47806		2.528(15)
$\angle N_1-C_{12}-C_{14}/^\circ$	92.391(84) <sup>d</sup>	92.56763	94.07465		
$\angle C_4-C_{12}-C_{14}/^\circ$	99.695(83) <sup>d</sup>	97.47748	102.23634	100.30(17)	
$\angle C_{12}-O_{13}-H_7/^\circ$	99.82(14) <sup>d</sup>	101.29623	99.72149		94.68(52)
$\angle C_2-H_7-O_{13}/^\circ$	131.42(14) <sup>d</sup>	129.44650	131.43521		128.4(15)
$\angle C_4-C_5-C_6-C_{12}/^\circ$	-0.53(13) <sup>d</sup>	4.00165	-1.97561		1.5(3.5)
$\angle C_5-C_6-C_{12}-C_{14}/^\circ$	126.079(75) <sup>d</sup>	117.38749	131.45448	122.4(2.1)	
$\gamma/^\circ$ <sup>f</sup>	75.23(36)				90.0

<sup>a</sup> The structural parameters of pyridine given in square brackets were fixed to the values reported in ref [22]. <sup>b</sup> The structural parameters of acetaldehyde given in square brackets were fixed to the values previously reported [A. Bauder, F. J. Lovas, and D. R. Johnson, *J. Phys. Chem. Ref. Data*, **1976**, 5, 53-77], except for methyl group which was fixed to a local C<sub>3</sub> symmetry to give a value of I<sub>a</sub>=3.20 uÅ<sup>2</sup>. <sup>c</sup> Standard errors in parenthesis in units of the last digit. <sup>d</sup> Derived values.

**Table S9.** (a) Comparison of the structural parameters derived from analysis of the internal rotation of the methyl group with those obtained from the  $r_0$ ,  $r_s$  or  $r_e$  (CCSD/6-311G(2d,p)) structures of pyridine-acetaldehyde (PY-AC) (see Figure 4). (b) Comparison of the experimental  $V_3$  internal rotation barrier values for PY-AC and free AC with the values of the parameters defining the three-fold potential energy functions for this motion calculated theoretically at MP2/aug-cc-pVTZ, CCSD/6-311++G(2d,p) and CCSD(T)/6-311++G(2d,p)//CCSD/6-311++G(2d,p). The three-fold potential energy function is given by:  $V(\alpha) = V_3(1 - \cos(\alpha + \tau))$  were  $\alpha$  is the internal rotation coordinate ( $\angle H_{16}C_{14}C_{12}O_{13}$ , see figures 3 and S1),  $\tau$  is the offset phase angle and  $V_3$  the three-fold barrier hindering the motion.

(a)				
Parameters <sup>a</sup>	Int. Rotation Analysis	$r_e$	$r_0$	$r_s$
$I_\alpha/\text{u}\text{\AA}^2$	3.20027 <sup>b</sup>	3.16	[3.200] <sup>b</sup>	-
$F_0/\text{GHz}$	157.9176	160.866	157.9309	-
$\delta/\text{rad}$	1.39284(76)	1.341	1.3842(21)	1.38124(78)
$\varepsilon/\text{rad}$	2.3610 (21)	2.406	2.36175(72)	2.4613(85)
$\angle(i,a)/^\circ$	79.804(43)	76.8	79.31(12)	79.139(45)
$\angle(i,b)/^\circ$	134.37(12)	136.2	134.321(36)	139.77(92)
$\angle(i,c)/^\circ$	46.16(12)	49.2	46.293(29)	45.77(36)

(b)				
	Exp.	MP2	CCSD	CCSD(T)
$V_3$ (PY-AC)/cm <sup>-1</sup>	343.60(32)	356.6	344.4	342.7
$\tau$ (PY-AC)/ <sup>c</sup>	-	7.1	4.0	4.0
$V_3$ (AC)/cm <sup>-1</sup>	407.59768 <sup>e</sup>	413.9	386.1	376.2
$\tau$ (AC)/ <sup>c</sup>	-	0	0	0
$\Delta V_3/\text{cm}^{-1}$	-64.0	-57.2	-41.7	-33.4

<sup>a</sup>  $I_\alpha$  is the moment of inertia of the methyl top.  $F_0$  is the methyl top internal rotational constant:  $F_0 = h/(8\pi^2 I_\alpha)$ .  $\angle(i,a)$ ,  $\angle(i,b)$ ,  $\angle(i,c)$  are the angles between the methyl top axis and the principal inertial axes,  $a$ ,  $b$  and  $c$ ;  $\delta$  is the angle of the internal rotation axis with the  $a$  inertial axis ( $\delta = \angle(i,a)$ ).  $\varepsilon$  is the angle between the principal inertial axis  $b$  and the projection of the internal rotation axis onto the  $bc$  plane.

<sup>b</sup> The fit of the spectrum in the global internal rotation analysis was done by assuming the  $I_\alpha$  in pyridine-acetaldehyde takes the same value as that determined for acetaldehyde [H. Maes, G. Włodarczak, D. Doucher and J. Demaison. *Z. Naturforsch*, **1987**, *42a*, 97-102]. In the  $r_0$  calculations, the structure of the methyl group was constrained to give this value.

<sup>c</sup> Taken from reference 24.

**Table S10.** The results of the NBO donor→acceptor intermolecular interactions analysis done for the equilibrium conformation of the complex pyridine-acetaldehyde, conformer A1, are given in the first two columns. The second order perturbation theory analysis of the Fock matrix in the NBO basis has been done at RHF/aug-cc-pVTZ level, for the structures optimized at CCSD/6-311++G(2d,p). The resulting donor→acceptor second order corrections ( $E^{(2)}$ ) and the stabilization energy calculated by deletion-type re-optimization ( $\Delta E_{\text{del}}$ ) are given. The most prominent interaction reflects the existence of an  $n \rightarrow \pi^*$  interaction ( $E^{(2)} = 8.9$  kJ/mol) stabilizing this conformer (see Figures 3 and S1 for atom labelling). The same calculations have been done for three additional points in the potential energy function for the methyl top internal rotation. Configuration labelled  $V_3$  correspond to one of the maxima in the methyl top internal rotation potential function  $V(\alpha)$  of PY-AC (see Figure 6) with values of the dihedral angle at  $\alpha = 56^\circ, 116^\circ$  or  $236^\circ$ . The other two points, labelled  $\alpha = 19^\circ$  and  $79^\circ$ , correspond respectively to configurations of the complex with minima ( $\alpha = 19^\circ, 139^\circ$  or  $259^\circ$ ) and maxima ( $\alpha = 79^\circ, 199^\circ$  or  $319^\circ$ ) of the difference function  $\Delta V(\alpha) = V_{\text{AC}} - V_{\text{Py-AC}}$  represented in Figure 6. Those configurations in turn correspond respectively to maximum or minimum values of the  $r(N_1 \cdots C_{12})$  distance (see Figures 6 and S5). These two configurations correspond, as shown in the table to the minimum and maximum values of the  $n \rightarrow \pi^*$  interaction energy along the  $r(N_1 \cdots C_{12})$  distance values sampled by the large amplitude oscillation geared to the internal rotation of the methyl group. The energy gain due to this  $n \rightarrow \pi^*$  interaction oscillation leads to a reduction of the barrier to internal rotation of the AC methyl group upon complexation.

Donor	Acceptor	A1 ( $\alpha = \angle H_{16}CCO = -4^\circ$ )		$V_3$ ( $\alpha=56^\circ$ )	( $\alpha=19^\circ$ )	( $\alpha=79^\circ$ )
		$E^{(2)}$ /kJ/mol	$\Delta E_{\text{del}}$ /kJ/mol	$\Delta E_{\text{del}}$ /kJ/mol	$\Delta E_{\text{del}}$ /kJ/mol	$\Delta E_{\text{del}}$ /kJ/mol
$n(N_1)$	$\pi^*(C_{12}-O_{13})$	8.9	6.7	8.1	5.5	9.8
$n(N_1)$	$\sigma^*(C_{14}-H_{16})$	-	-	0.9	-	1.3
$n(N_1)$	$\sigma^*(C_{14}-H_{17})$	0.3	0.2	-	0.5	-
$n(N_1)$	$\sigma^*(C_{14}-H_{18})$	0.4	0.3	-	-	-
$\pi(C_{12}-O_{13})$	$\sigma^*(C_2-C_3)$	0.9	0.9	0.9	0.8	1.0
$\pi(C_{12}-O_{13})$	$\sigma^*(C_2-H_7)$	1.2	1.1	1.1	1.1	1.1
$\pi(C_{12}-O_{13})$	$\sigma^*(N_1-C_6)$	0.3	0.3	0.3	0.3	0.4
$n(1) (O_{13})$	$\sigma^*(C_2-H_7)$	0.7	0.7	0.6	0.7	0.6

**Table S11.** Observed frequencies,  $\nu_A$  (MHz), for the A torsional state of the parent species of the pyridine-acetaldehyde complex and residuals from the semirigid rotor fit (o-c/MHz) or the internal rotation analysis (o-c (XIAM)/MHz).

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	$\nu_A$	o-c	o-c (XIAM)
2	1	2	2		1	1	1	1	2781.217	-0.001	0.000
2	1	2	2		1	1	1	2	2781.485	0.003	0.004
2	1	2	3		1	1	1	2	2782.487	-0.003	-0.003
2	1	2	1		1	1	1	1	2782.787	-0.001	0.001
2	1	2	1		1	1	1	0	2783.443	-0.003	-0.002
2	0	2	2		1	0	1	2	2888.367	-0.007	-0.007
2	0	2	1		1	0	1	0	2888.592	-0.003	-0.003
2	0	2	3		1	0	1	2	2889.679	0.001	0.001
2	0	2	1		1	0	1	1	2891.604	-0.003	-0.002
1	1	0	1		1	0	1	0	2964.578	0.004	0.001
1	1	0	0		1	0	1	1	2965.234	0.001	-0.002
1	1	0	2		1	0	1	2	2965.443	0.003	0.000
1	1	0	1		1	0	1	2	2966.391	0.010	0.007
1	1	0	2		1	0	1	1	2966.656	0.012	0.009
1	1	0	1		1	0	1	1	2967.590	0.005	0.002
2	1	1	2		1	1	0	1	3002.228	-0.007	-0.006
2	1	1	1		1	1	0	1	3002.670	-0.005	-0.004
2	1	1	2		1	1	0	2	3003.174	-0.002	-0.002
2	1	1	3		1	1	0	2	3003.458	0.001	0.000
2	1	1	1		1	1	0	0	3005.031	0.004	0.005
2	1	1	1		2	0	2	1	3078.648	-0.005	-0.008
2	1	1	2		2	0	2	3	3078.936	-0.002	-0.005
2	1	1	3		2	0	2	3	3079.212	-0.008	-0.011
2	1	1	2		2	0	2	2	3080.235	-0.007	-0.011
4	0	4	4		3	1	3	3	3161.323	-0.002	0.026
4	0	4	5		3	1	3	4	3161.323	-0.002	-0.020
3	1	2	2		3	0	3	2	3255.354	0.025	0.021
3	1	2	4		3	0	3	4	3255.605	0.017	0.013
3	1	2	3		3	0	3	3	3256.347	0.019	0.015
4	1	3	3		4	0	4	3	3501.298	0.014	0.010
4	1	3	5		4	0	4	5	3501.464	0.016	0.011
4	1	3	4		4	0	4	4	3502.114	0.025	0.020
5	1	4	4		5	0	5	4	3825.390	0.017	0.013
5	1	4	6		5	0	5	6	3825.518	0.022	0.017
5	1	4	5		5	0	5	5	3826.118	0.015	0.011
3	1	3	3		2	1	2	3	4170.104	-0.007	-0.007
3	1	3	3		2	1	2	2	4171.115	-0.004	-0.004
3	1	3	2		2	1	2	1	4171.421	0.001	0.001
3	1	3	4		2	1	2	3	4171.492	-0.004	-0.003
3	1	3	2		2	1	2	2	4172.988	-0.001	0.000
6	1	5	5		6	0	6	5	4237.503	-0.006	-0.010
6	1	5	7		6	0	6	7	4237.598	-0.013	-0.017

**Table S11.** (continued 1).

J'	K'a	K'c	F'	←	J''	K''a	K''c	F''	vA	o-c	o-c (XIAM)
6	1	5	6	6	0	6	6	4238.204	-0.008	-0.012	
1	1	1	0	0	0	0	1	4301.220	-0.001	-0.003	
1	1	1	2	0	0	0	1	4301.617	0.000	-0.002	
1	1	1	1	0	0	0	1	4301.877	-0.003	-0.006	
3	0	3	3	2	0	2	3	4325.188	-0.006	-0.005	
3	0	3	2	2	0	2	1	4326.323	0.001	0.001	
3	0	3	3	2	0	2	2	4326.470	-0.028	-0.028	
3	0	3	4	2	0	2	3	4326.565	-0.001	-0.001	
3	0	3	2	2	0	2	2	4328.353	0.002	0.002	
3	2	2	3	2	2	1	2	4338.047	-0.004	-0.004	
3	2	2	2	2	2	1	2	4338.047	-0.004	-0.004	
3	2	2	4	2	2	1	3	4339.339	-0.003	-0.003	
3	2	2	3	2	2	1	3	4339.339	-0.003	-0.003	
3	2	2	2	2	2	1	1	4340.057	-0.002	-0.001	
3	2	1	3	2	2	0	2	4350.625	-0.006	-0.006	
3	2	1	4	2	2	0	3	4351.898	-0.002	-0.003	
3	2	1	2	2	2	0	1	4352.615	0.001	0.001	
3	1	2	3	2	1	1	3	4502.302	-0.001	-0.001	
3	1	2	3	2	1	1	2	4502.583	-0.002	-0.003	
3	1	2	4	2	1	1	3	4502.929	-0.005	-0.006	
3	1	2	2	2	1	1	1	4503.000	0.003	0.002	
3	1	2	2	2	1	1	2	4503.441	0.002	0.003	
7	1	6	6	7	0	7	6	4747.725	-0.002	-0.003	
7	1	6	8	7	0	7	8	4747.817	0.003	0.001	
7	1	6	7	7	0	7	7	4748.420	-0.004	-0.006	
5	0	5	4	4	1	4	3	4772.476	-0.005	-0.004	
5	0	5	6	4	1	4	5	4772.574	-0.005	-0.004	
5	0	5	5	4	1	4	4	4772.647	-0.004	-0.003	
8	1	7	9	8	0	8	9	5364.895	0.023	0.026	
8	1	7	7	8	0	8	7	5364.810	0.017	0.021	
4	1	4	4	3	1	3	4	5556.762	-0.001	0.000	
4	1	4	4	3	1	3	3	5558.147	-0.001	0.000	
4	1	4	3	3	1	3	2	5558.237	-0.001	0.000	
4	1	4	5	3	1	3	4	5558.322	0.000	0.000	
4	1	4	3	3	1	3	3	5560.090	-0.018	-0.017	
2	1	2	1	1	0	1	0	5636.284	-0.003	-0.005	
2	1	2	2	1	0	1	2	5636.524	-0.002	-0.004	
2	1	2	3	1	0	1	2	5637.531	-0.003	-0.005	
2	1	2	2	1	0	1	1	5637.729	-0.001	-0.003	
2	1	2	1	1	0	1	1	5639.297	-0.002	-0.004	
4	0	4	4	3	0	3	4	5752.700	0.000	0.000	
4	0	4	3	3	0	3	2	5754.017	-0.002	-0.001	

**Table S11.** (continued 2).

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	o-c (XIAM)
4	0	4	4	3	0	3	3	5754.073	0.000	0.001	
4	0	4	5	3	0	3	4	5754.132	0.000	0.001	
4	0	4	3	3	0	3	3	5755.868	-0.004	-0.004	
4	2	3	4	3	2	2	3	5782.510	-0.005	-0.004	
4	2	3	4	3	2	2	4	5782.510	-0.005	-0.004	
4	2	3	5	3	2	2	4	5783.059	-0.007	-0.006	
4	2	3	3	3	2	2	2	5783.202	-0.005	-0.005	
4	2	3	3	3	2	2	3	5783.202	-0.005	-0.005	
4	2	2	4	3	2	1	3	5813.831	-0.005	-0.005	
4	2	2	5	3	2	1	4	5814.355	-0.003	-0.004	
4	2	2	3	3	2	1	2	5814.491	-0.005	-0.006	
4	1	3	4	3	1	2	4	5999.203	0.002	0.001	
4	1	3	3	3	1	2	2	5999.973	0.000	0.000	
4	1	3	4	3	1	2	3	5999.835	0.002	0.002	
4	1	3	5	3	1	2	4	5999.994	0.003	0.002	
4	1	3	3	3	1	2	3	6000.822	-0.004	-0.004	
6	0	6	5	5	1	5	4	6400.786	-0.007	-0.006	
6	0	6	7	5	1	5	6	6400.865	-0.006	-0.005	
6	0	6	6	5	1	5	5	6400.980	-0.008	-0.007	
3	1	3	3	2	0	2	3	6917.965	-0.003	-0.004	
3	1	3	2	2	0	2	1	6919.117	0.004	0.003	
3	1	3	3	2	0	2	2	6919.272	0.000	-0.001	
3	1	3	4	2	0	2	3	6919.355	0.003	0.002	
3	1	3	2	2	0	2	2	6921.142	0.000	-0.001	
5	1	5	5	4	1	4	5	6940.611	-0.001	-0.001	
5	1	5	5	4	1	4	4	6942.170	-0.001	0.000	
5	1	5	4	4	1	4	3	6942.208	-0.001	-0.001	
5	1	5	6	4	1	4	5	6942.272	-0.001	0.000	
5	1	5	4	4	1	4	4	6944.167	-0.003	-0.003	
5	0	5	5	4	0	4	5	7168.067	-0.002	-0.002	
5	0	5	4	4	0	4	3	7169.490	-0.006	-0.001	
5	0	5	5	4	0	4	4	7169.490	-0.006	-0.009	
5	0	5	6	4	0	4	5	7169.546	-0.010	-0.009	
5	0	5	4	4	0	4	4	7171.279	-0.011	-0.011	
5	2	4	5	4	2	3	4	7224.441	-0.009	-0.008	
5	2	4	6	4	2	3	5	7224.708	-0.033	-0.032	
5	2	4	4	4	2	3	3	7224.771	0.000	0.001	
5	3	3	5	4	3	2	4	7241.368	-0.006	-0.006	
5	3	3	6	4	3	2	5	7241.983	-0.003	-0.003	
5	3	3	4	4	3	2	3	7242.130	-0.007	-0.007	
5	3	2	5	4	3	1	4	7242.541	-0.007	-0.007	
5	3	2	6	4	3	1	5	7243.150	-0.009	-0.009	

**Table S11.** (continued 3).

J'	K'a	K'c	F'	←	J''	K''a	K''c	F''	vA	o-c	o-c (XIAM)
5	3	2	4	4	3	1	3	7243.300	-0.010	-0.010	
5	2	3	5	4	2	2	4	7286.611	-0.006	-0.007	
5	2	3	6	4	2	2	5	7286.859	-0.015	-0.015	
5	2	3	4	4	2	2	3	7286.911	0.012	0.011	
9	2	7	10	9	1	8	10	7336.565	-0.006	-0.008	
9	2	7	9	9	1	8	9	7336.622	-0.011	-0.013	
8	2	6	7	8	1	7	7	7450.239	-0.004	0.002	
8	2	6	9	8	1	7	9	7450.239	-0.004	-0.003	
5	1	4	5	4	1	3	4	7493.516	0.003	0.003	
5	1	4	4	4	1	3	3	7493.583	0.002	0.002	
5	1	4	6	4	1	3	5	7493.608	0.003	0.003	
5	1	4	4	4	1	3	4	7494.563	-0.012	-0.011	
7	2	5	8	7	1	6	8	7615.600	-0.006	0.000	
6	2	4	5	6	1	5	5	7813.677	-0.010	0.005	
6	2	4	7	6	1	5	7	7813.677	-0.010	-0.005	
6	2	4	6	6	1	5	6	7813.738	-0.015	-0.006	
4	1	4	4	3	0	3	3	8150.923	0.002	0.001	
4	1	4	3	3	0	3	2	8151.028	-0.001	-0.002	
4	1	4	5	3	0	3	4	8151.110	0.001	0.001	
4	1	4	3	3	0	3	4	8151.509	-0.001	-0.001	
6	1	6	6	5	1	5	5	8322.735	0.000	0.000	
6	1	6	5	5	1	5	4	8322.757	0.001	0.000	
6	1	6	7	5	1	5	6	8322.803	0.000	-0.001	
6	0	6	6	5	0	5	5	8570.507	-0.001	0.000	
6	0	6	5	5	0	5	4	8570.523	0.001	0.001	
6	0	6	7	5	0	5	6	8570.563	0.000	0.000	
6	2	5	6	5	2	4	5	8663.614	0.001	0.002	
6	2	5	7	5	2	4	6	8663.791	0.001	0.002	
6	2	5	7	5	2	4	6	8663.791	0.001	0.002	
6	3	4	6	5	3	3	5	8693.322	0.000	0.000	
6	3	4	7	5	3	3	6	8693.681	0.002	0.001	
6	3	4	5	5	3	3	4	8693.738	0.002	0.002	
6	3	3	6	5	3	2	5	8696.448	0.002	0.002	
6	3	3	7	5	3	2	6	8696.802	0.000	0.000	
6	3	3	5	5	3	2	4	8696.859	0.002	0.002	
6	2	4	6	5	2	3	5	8770.985	0.002	0.001	
6	2	4	5	5	2	3	4	8771.123	0.005	0.006	
6	2	4	7	5	2	3	6	8771.123	0.005	0.003	
6	1	5	6	5	1	4	5	8982.618	0.002	0.003	
6	1	5	5	5	1	4	4	8982.658	0.001	0.001	
6	1	5	7	5	1	4	6	8982.679	0.001	0.001	

**Table S11.** (continued 4).

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	o-c (XIAM)
5	1	5	5	4	0	4	4	9339.020	0.001	0.000	
5	1	5	4	4	0	4	3	9339.218	-0.001	-0.002	
5	1	5	6	4	0	4	5	9339.249	0.000	-0.001	
7	1	7	7	6	1	6	6	9699.452	0.000	-0.002	
7	1	7	6	6	1	6	5	9699.467	0.000	-0.002	
7	1	7	8	6	1	6	7	9699.503	0.001	-0.001	
7	0	7	7	6	0	6	6	9955.722	0.002	0.002	
7	0	7	6	6	0	6	5	9955.746	-0.001	-0.002	
7	0	7	8	6	0	6	7	9955.776	-0.001	-0.002	
7	2	6	7	6	2	5	6	10099.553	-0.002	-0.001	
7	2	6	6	6	2	5	5	10099.661	-0.004	-0.003	
7	2	6	8	6	2	5	7	10099.674	0.000	0.002	
7	3	5	7	6	3	4	6	10146.548	0.000	0.000	
7	3	5	8	6	3	4	7	10146.775	0.000	0.000	
7	3	5	6	6	3	4	5	10146.796	0.000	0.000	
7	3	4	7	6	3	3	6	10153.555	0.001	0.001	
7	3	4	8	6	3	3	7	10153.778	0.001	0.001	
7	3	4	6	6	3	3	5	10153.797	0.000	-0.001	
7	2	5	7	6	2	4	6	10267.824	0.001	0.000	
7	2	5	6	6	2	4	5	10267.885	0.001	0.000	
7	2	5	8	6	2	4	7	10267.897	0.001	0.000	
7	1	6	7	6	1	5	6	10465.931	-0.002	0.000	
7	1	6	6	6	1	5	5	10465.962	-0.002	0.000	
7	1	6	8	6	1	5	7	10465.977	-0.003	-0.002	
6	1	6	6	5	0	5	5	10492.255	0.000	-0.001	
6	1	6	5	5	0	5	4	10492.485	0.001	-0.001	
6	1	6	7	5	0	5	6	10492.497	0.001	0.000	

**Table S12.** Observed frequencies,  $\nu_E$  (MHz), for the E torsional state of the parent species of the pyridine-acetaldehyde complex and residuals from the semirigid rotor fit (o-c/MHz) or the internal rotation analysis (o-c (XIAM) /MHz). The last line give the magnitude of the internal rotation splittings  $\nu_A - \nu_E$ .

$J'$	$K'_a$	$K'_c$	$F'$	$\leftarrow$	$J''$	$K''_a$	$K''_c$	$F''$	$\nu_E$	o-c	o-c (XIAM)	$\nu_A - \nu_E$
2	1	2	2		1	1	1	1	2781.217	0.004	0.005	0.000
2	1	2	2		1	1	1	2	2781.485	0.008	0.008	0.000
2	1	2	3		1	1	1	2	2782.487	0.001	0.001	0.000
2	1	2	1		1	1	1	1	2782.787	0.004	0.005	0.000
2	1	2	1		1	1	1	0	2783.443	0.001	0.002	0.000
2	0	2	2		1	0	1	2	2888.298	-0.007	-0.006	-0.068
2	0	2	1		1	0	1	0	2888.519	-0.008	-0.006	-0.073
2	0	2	2		1	0	1	1	2889.508	-0.002	-0.001	
2	0	2	3		1	0	1	2	2889.607	-0.003	-0.001	-0.072
2	0	2	1		1	0	1	1	2891.535	-0.005	-0.003	-0.070
1	1	0	1		1	0	1	0	2964.656	0.007	0.007	0.079
1	1	0	0		1	0	1	1	2965.315	0.005	0.005	0.081
1	1	0	2		1	0	1	2	2965.517	0.000	0.001	0.074
1	1	0	1		1	0	1	2	2966.469	0.012	0.013	0.078
1	1	0	2		1	0	1	1	2966.726	0.005	0.006	0.070
2	1	1	2		1	1	0	1	3002.110	-0.009	-0.009	-0.118
2	1	1	3		1	1	0	2	3003.340	-0.002	-0.002	-0.118
2	1	1	1		1	1	0	0	3004.912	0.001	0.002	-0.119
2	1	1	1		2	0	2	1	3078.704	0.022	0.022	0.056
2	1	1	3		2	0	2	3	3079.265	0.016	0.015	0.052
2	1	1	2		2	0	2	2	3080.283	0.013	0.012	0.049
4	0	4	4		3	1	3	3	3161.147	0.004	0.007	-0.177
4	0	4	5		3	1	3	4	3161.194	0.005	0.008	-0.129
3	1	2	2		3	0	3	2	3255.354	0.003	0.002	0.000
3	1	2	4		3	0	3	4	3255.605	-0.005	-0.007	0.000
3	1	2	3		3	0	3	3	3256.347	-0.004	-0.005	0.000
4	1	3	3		4	0	4	3	3501.298	-0.010	-0.011	0.000
4	1	3	5		4	0	4	5	3501.464	-0.008	-0.010	0.000
4	1	3	4		4	0	4	4	3502.114	0.000	-0.001	0.000
5	1	4	4		5	0	5	4	3825.390	-0.013	-0.011	0.000
5	1	4	6		5	0	5	6	3825.518	-0.008	-0.007	0.000
5	1	4	5		5	0	5	5	3826.118	-0.015	-0.014	0.000
3	1	3	3		2	1	2	3	4170.036	-0.005	-0.005	-0.068
3	1	3	3		2	1	2	2	4171.043	-0.006	-0.006	-0.072
3	1	3	2		2	1	2	1	4171.343	-0.007	-0.007	-0.078
3	1	3	4		2	1	2	3	4171.421	-0.005	-0.005	-0.071
3	1	3	2		2	1	2	2	4172.914	-0.005	-0.004	-0.074
6	1	5	5		6	0	6	5	4237.562	0.016	0.021	0.059
6	1	5	7		6	0	6	7	4237.659	0.011	0.016	0.061
6	1	5	6		6	0	6	6	4238.255	0.007	0.011	0.052
1	1	1	0		0	0	0	1	4301.103	-0.008	-0.006	-0.117

**Table S12.** (continued)

J'	K'a	K'c	F'	←	J''	K''a	K''c	F''	v_E	o-c	o-c (XIAM)	v_A-v_E
1	1	1	2	0	0	0	1	4301.502	-0.004	-0.003	-0.115	
1	1	1	1	0	0	0	1	4301.764	-0.006	-0.005	-0.112	
3	0	3	3	2	0	2	3	4325.087	-0.005	-0.003	-0.101	
3	0	3	2	2	0	2	1	4326.220	0.001	0.002	-0.102	
3	0	3	3	2	0	2	2	4326.392	-0.003	-0.002		
3	0	3	4	2	0	2	3	4326.470	0.006	0.007	-0.095	
3	0	3	2	2	0	2	2	4328.249	0.000	0.002	-0.104	
3	1	2	3	2	1	1	3	4502.190	-0.003	-0.003	-0.112	
3	1	2	3	2	1	1	2	4502.472	-0.003	-0.003	-0.111	
3	1	2	4	2	1	1	3	4502.821	-0.004	-0.003	-0.108	
3	1	2	2	2	1	1	1	4502.883	-0.006	-0.006	-0.118	
3	1	2	2	2	1	1	2	4503.326	-0.003	-0.002	-0.115	
7	1	6	6	7	0	7	6	4747.763	-0.004	-0.001	0.038	
7	1	6	8	7	0	7	8	4747.864	0.008	0.012	0.047	
7	1	6	7	7	0	7	7	4748.461	-0.004	-0.001	0.041	
5	0	5	4	4	1	4	3	4772.253	-0.003	-0.002	-0.223	
5	0	5	6	4	1	4	5	4772.351	-0.003	-0.002	-0.223	
5	0	5	5	4	1	4	4	4772.422	-0.004	-0.003	-0.225	
8	1	7	9	8	0	8	9	5364.895	-0.016	-0.027		
8	1	7	7	8	0	8	7	5364.810	-0.022	-0.032		
4	1	4	4	3	1	3	4	5556.658	-0.001	-0.001	-0.104	
4	1	4	4	3	1	3	3	5558.044	0.000	0.000	-0.103	
4	1	4	3	3	1	3	2	5558.134	-0.001	-0.001	-0.103	
4	1	4	5	3	1	3	4	5558.214	-0.004	-0.004	-0.107	
4	1	4	3	3	1	3	3	5560.003	-0.002	0.000	-0.086	
2	1	2	1	1	0	1	0	5636.199	-0.008	-0.008	-0.086	
2	1	2	2	1	0	1	2	5636.439	-0.006	-0.005	-0.085	
2	1	2	3	1	0	1	2	5637.448	-0.005	-0.005	-0.083	
2	1	2	2	1	0	1	1	5637.645	-0.004	-0.004	-0.084	
2	1	2	1	1	0	1	1	5639.213	-0.006	-0.005	-0.084	
4	0	4	4	3	0	3	4	5752.563	0.000	0.000	-0.138	
4	0	4	3	3	0	3	2	5753.883	0.002	0.002	-0.134	
4	0	4	4	3	0	3	3	5753.938	0.002	0.002	-0.135	
4	0	4	5	3	0	3	4	5753.996	0.002	0.002	-0.135	
4	0	4	3	3	0	3	3	5755.734	-0.001	-0.001	-0.134	
4	2	3	4	3	2	2	3	5783.599	-0.020	-0.017	1.089	
4	2	3	5	3	2	2	4	5784.161	-0.011	-0.009	1.102	
4	2	3	3	3	2	2	2	5784.293	-0.021	-0.019	1.091	
4	2	2	4	3	2	1	3	5812.470	-0.013	-0.015	-1.361	
4	2	2	5	3	2	1	4	5812.997	-0.007	-0.009	-1.359	
4	2	2	3	3	2	1	2	5813.131	-0.009	-0.011	-1.360	

**Table S12.** (continued)

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>E</sub>	o-c	o-c (XIAM)	v <sub>A</sub> -v <sub>E</sub>
4	1	3	4	3	1	2	4	5999.065	-0.002	-0.001	-0.138	
4	1	3	3	3	1	2	2	5999.835	-0.003	-0.002	-0.138	
4	1	3	4	3	1	2	3	5999.699	0.000	0.001	-0.136	
4	1	3	5	3	1	2	4	5999.855	-0.001	0.000	-0.138	
4	1	3	3	3	1	2	3	6000.688	-0.004	-0.003	-0.135	
6	0	6	5	5	1	5	4	6400.484	-0.005	-0.007	-0.303	
6	0	6	7	5	1	5	6	6400.564	-0.003	-0.004	-0.301	
6	0	6	6	5	1	5	5	6400.682	-0.002	-0.003	-0.298	
3	1	3	3	2	0	2	3	6917.880	-0.005	-0.006	-0.086	
3	1	3	2	2	0	2	1	6919.035	0.005	0.004	-0.082	
3	1	3	3	2	0	2	2	6919.193	0.004	0.003	-0.079	
3	1	3	4	2	0	2	3	6919.272	0.003	0.002	-0.084	
3	1	3	2	2	0	2	2	6921.054	-0.004	-0.004	-0.087	
5	1	5	5	4	1	4	5	6940.482	-0.001	0.000	-0.129	
5	1	5	5	4	1	4	4	6942.043	0.001	0.002	-0.127	
5	1	5	4	4	1	4	3	6942.079	-0.002	-0.001	-0.129	
5	1	5	6	4	1	4	5	6942.144	0.000	0.001	-0.128	
5	1	5	4	4	1	4	4	6944.048	0.006	0.008	-0.119	
5	0	5	5	4	0	4	5	7167.898	0.001	0.000	-0.169	
5	0	5	4	4	0	4	3	7169.320	0.002	0.001	-0.170	
5	0	5	5	4	0	4	4	7169.332	0.004	0.003	-0.159	
5	0	5	6	4	0	4	5	7169.386	0.003	0.002	-0.160	
5	0	5	4	4	0	4	4	7171.111	-0.007	-0.008	-0.168	
5	2	4	5	4	2	3	4	7224.708	0.007	0.008	0.268	
5	2	4	6	4	2	3	5	7224.981	-0.012	-0.011	0.273	
5	2	4	4	4	2	3	3	7225.029	0.006	0.007	0.258	
5	3	3	5	4	3	2	4	7241.798	-0.007	0.021	0.430	
5	3	3	6	4	3	2	5	7242.408	-0.009	0.018	0.425	
5	3	2	5	4	3	1	4	7241.798	-0.007	-0.034	-0.138	
5	3	2	6	4	3	1	5	7242.408	-0.009	-0.036	-0.138	
5	2	3	5	4	2	2	4	7286.046	-0.007	-0.008	-0.743	
5	2	3	6	4	2	2	5	7286.292	-0.016	-0.017	-0.743	
5	2	3	4	4	2	2	3	7286.346	0.012	0.011	-0.565	
9	2	7	10	9	1	8	10	7336.622	-0.004	-0.010	-0.566	
9	2	7	9	9	1	8	9	7336.688	0.000	-0.006	-0.565	
8	2	6	7	8	1	7	7	7450.323	0.010	0.017	0.057	
8	2	6	9	8	1	7	9	7450.323	0.005	0.012	0.066	
5	1	4	5	4	1	3	4	7493.347	0.000	0.001	0.084	
5	1	4	4	4	1	3	3	7493.415	0.000	0.002	0.084	
5	1	4	6	4	1	3	5	7493.439	0.000	0.002	-0.169	
5	1	4	4	4	1	3	4	7494.388	-0.020	-0.018	-0.168	

**Table S12.** (continued)

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>E</sub>	o-c	o-c (XIAM)	v <sub>A</sub> -v <sub>E</sub>
7	2	5	8	7	1	6	8	7615.690	-0.019	-0.003	0.090	
6	2	4	5	6	1	5	5	7813.835	-0.011	0.010	0.157	
6	2	4	7	6	1	5	7	7813.835	-0.021	-0.001	0.157	
6	2	4	6	6	1	5	6	7813.887	-0.029	-0.009	0.149	
4	1	4	4	3	0	3	3	8150.841	0.004	0.002	-0.082	
4	1	4	3	3	0	3	2	8150.945	0.001	-0.001	-0.082	
4	1	4	5	3	0	3	4	8151.028	0.004	0.002	-0.082	
6	1	6	6	5	1	5	5	8322.586	0.000	0.001	-0.149	
6	1	6	5	5	1	5	4	8322.607	0.000	0.001	-0.150	
6	1	6	7	5	1	5	6	8322.653	0.000	0.000	-0.150	
6	0	6	6	5	0	5	5	8570.302	0.002	0.001	-0.205	
6	0	6	5	5	0	5	4	8570.316	0.002	0.001	-0.207	
6	0	6	7	5	0	5	6	8570.359	0.003	0.001	-0.204	
6	2	5	6	5	2	4	5	8663.584	0.001	0.002	-0.030	
6	2	5	7	5	2	4	6	8663.760	0.001	0.001	-0.031	
6	2	5	7	5	2	4	6	8663.760	0.001	0.001	-0.031	
6	3	4	6	5	3	3	5	8694.430	0.001	-0.001	1.109	
6	3	4	7	5	3	3	6	8694.788	0.002	0.000	1.107	
6	3	4	5	5	3	3	4	8694.845	0.003	0.000	1.107	
6	3	3	6	5	3	2	5	8694.963	-0.001	0.002	-1.485	
6	3	3	7	5	3	2	6	8695.318	-0.001	0.001	-1.483	
6	3	3	5	5	3	2	4	8695.374	-0.001	0.001	-1.485	
6	2	4	6	5	2	3	5	8770.638	0.002	0.001	-0.348	
6	2	4	5	5	2	3	4	8770.774	0.005	0.004	-0.349	
6	2	4	7	5	2	3	6	8770.774	0.002	0.001	-0.349	
6	1	5	6	5	1	4	5	8982.416	0.000	0.002	-0.203	
6	1	5	5	5	1	4	4	8982.456	-0.001	0.000	-0.203	
6	1	5	7	5	1	4	6	8982.476	-0.002	0.000	-0.203	
5	1	5	5	4	0	4	4	9338.946	0.002	0.001	-0.074	
5	1	5	4	4	0	4	3	9339.144	0.000	-0.001	-0.074	
5	1	5	6	4	0	4	5	9339.174	0.001	0.000	-0.075	
7	1	7	7	6	1	6	6	9699.286	0.001	-0.001	-0.166	
7	1	7	6	6	1	6	5	9699.301	0.001	-0.001	-0.166	
7	1	7	8	6	1	6	7	9699.338	0.003	0.001	-0.165	
7	0	7	7	6	0	6	6	9955.476	-0.003	0.000	-0.246	
7	0	7	6	6	0	6	5	9955.505	-0.002	0.001	-0.241	
7	0	7	8	6	0	6	7	9955.533	-0.004	-0.001	-0.243	
7	2	6	7	6	2	5	6	10099.408	0.000	-0.001	-0.145	
7	2	6	6	6	2	5	5	10099.517	-0.001	-0.001	-0.144	
7	2	6	8	6	2	5	7	10099.527	0.001	0.001	-0.146	
7	3	5	7	6	3	4	6	10148.380	0.001	0.000	1.832	

**Table S12.** (continued)

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>E</sub>	o-c	o-c (XIAM)	v <sub>A</sub> -v <sub>E</sub>
7	3	5	8	6	3	4	7	10148.607	0.002	0.000	0.000	1.832
7	3	5	6	6	3	4	5	10148.627	0.001	-0.001	-0.001	1.831
7	3	4	7	6	3	3	6	10151.284	0.000	0.000	0.000	-2.271
7	3	4	8	6	3	3	7	10151.508	0.001	0.001	0.001	-2.271
7	3	4	6	6	3	3	5	10151.525	-0.002	-0.002	-0.002	-2.272
7	2	5	7	6	2	4	6	10267.528	0.002	-0.001	-0.001	-0.296
7	2	5	6	6	2	4	5	10267.588	0.001	-0.002	-0.002	-0.297
7	2	5	8	6	2	4	7	10267.600	0.002	-0.001	-0.001	-0.296
7	1	6	7	6	1	5	6	10465.695	-0.001	0.000	0.000	-0.236
7	1	6	6	6	1	5	5	10465.726	-0.003	-0.001	-0.001	-0.237
7	1	6	8	6	1	5	7	10465.740	-0.004	-0.002	-0.002	-0.237
6	1	6	6	5	0	5	5	10492.200	-0.002	-0.001	-0.001	-0.055
6	1	6	5	5	0	5	4	10492.428	-0.004	-0.003	-0.003	-0.057
6	1	6	7	5	0	5	6	10492.441	-0.002	-0.001	-0.001	-0.056

**Table S13.** Observed frequencies (MHz) for the <sup>13</sup>C<sub>2</sub> species of pyridine-formaldehyde complex (see Figures 3 and S1 for labelling)

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	v <sub>E</sub>	o-c
4	1	4	4	3	1	3	3	5552.205	0.001	5552.099	-0.002	
4	1	4	3	3	1	3	2	5552.294	-0.001	5552.192	-0.001	
4	1	4	5	3	1	3	4	5552.380	0.001	5552.277	0.001	
4	0	4	3	3	0	3	2	5748.760	-0.001	5748.625	-0.001	
4	0	4	4	3	0	3	3	5748.815	0.000	5748.680	0.001	
4	0	4	5	3	0	3	4	5748.875	0.002	5748.739	0.000	
4	1	3	3	3	1	2	2	5996.209	0.001	5996.076	0.003	
4	1	3	4	3	1	2	3	5996.066	-0.002	5995.933	0.000	
4	1	3	5	3	1	2	4	5996.227	0.001	5996.091	0.000	
5	1	5	5	4	1	4	4	6934.657	0.001	6934.530	0.001	
5	1	5	4	4	1	4	3	6934.693	-0.001	6934.566	-0.001	
5	1	5	6	4	1	4	5	6934.758	0.000	6934.630	0.000	
5	0	5	4	4	0	4	3	7162.557	0.000	7162.387	-0.001	
5	0	5	5	4	0	4	4	7162.565	-0.001	7162.398	0.001	
5	0	5	6	4	0	4	5	7162.622	0.000	7162.453	0.000	
5	1	4	5	4	1	3	4	7488.701	-0.001	7488.534	0.000	
5	1	4	4	4	1	3	3	7488.768	0.000	7488.601	-0.001	
5	1	4	6	4	1	3	5	7488.793	0.001	7488.625	-0.001	

**Table S14.** Observed frequencies (MHz) for the  $^{13}\text{C}_3$  species of pyridine-formaldehyde complex (see Figures 3 and S1 for labelling)

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	v <sub>E</sub>	o-c
4	1	4	4	←	3	1	3	3	5522.885	0.000	5522.783	0.000
4	1	4	3	←	3	1	3	2	5522.976	0.000	5522.873	-0.001
4	1	4	5	←	3	1	3	4	5523.060	0.001	5522.957	0.000
4	0	4	3	←	3	0	3	2	5718.978	0.002	5718.840	-0.001
4	0	4	4	←	3	0	3	3	5719.026	-0.004	5718.894	0.000
4	0	4	5	←	3	0	3	4	5719.088	-0.001	5718.954	0.001
4	1	3	3	←	3	1	2	2	5966.209	0.002	5966.066	-0.004
4	1	3	4	←	3	1	2	3	5966.066	-0.002	5965.933	0.004
4	1	3	5	←	3	1	2	4	5966.226	0.000	5966.091	0.002
5	1	5	5	←	4	1	4	4	6897.981	0.000	6897.855	0.001
5	1	5	4	←	4	1	4	3	6898.017	-0.003	6897.896	0.002
5	1	5	6	←	4	1	4	5	6898.084	0.002	6897.957	0.001
5	0	5	4	←	4	0	4	3	7125.214	-0.002	7125.046	-0.002
5	0	5	5	←	4	0	4	4	7125.226	0.002	7125.057	0.001
5	0	5	6	←	4	0	4	5	7125.282	0.001	7125.113	0.000

**Table S15.** Observed frequencies (MHz) for the  $^{13}\text{C}_4$  species of pyridine-formaldehyde complex (see Figures 3 and S1 for labelling).

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	v <sub>E</sub>	o-c
4	1	4	4	←	3	1	3	3	5493.790	0.001	5493.688	-0.001
4	1	4	3	←	3	1	3	2	5493.881	0.001	5493.778	-0.002
4	1	4	5	←	3	1	3	4	5493.964	0.000	5493.864	0.000
4	0	4	3	←	3	0	3	2	5685.812	-0.003	5685.681	-0.001
4	0	4	4	←	3	0	3	3	5685.869	-0.001	5685.737	0.001
4	0	4	5	←	3	0	3	4	5685.928	0.000	5685.794	0.000
4	1	3	3	←	3	1	2	2	5925.641	0.001	5925.510	0.002
4	1	3	4	←	3	1	2	3	5925.499	-0.001	5925.367	-0.002
4	1	3	5	←	3	1	2	4	5925.661	0.002	5925.525	-0.002
5	1	5	5	←	4	1	4	4	6861.970	0.001	6861.843	-0.001
5	1	5	4	←	4	1	4	3	6862.007	-0.001	6861.880	-0.003
5	1	5	6	←	4	1	4	5	6862.073	0.002	6861.948	0.002
3	1	3	2	←	2	0	2	1	6878.078	0.002		
3	1	3	3	←	2	0	2	2	6878.237	0.001	6878.155	-0.001
3	1	3	4	←	2	0	2	3	6878.314	-0.003	6878.237	0.001
5	0	5	4	←	4	0	4	3	7085.268	-0.002	7085.103	0.001
5	0	5	5	←	4	0	4	4	7085.281	0.002	7085.114	0.003
5	0	5	6	←	4	0	4	5	7085.335	0.000	7085.169	0.002

**Table S16.** Observed frequencies (MHz) for the  $^{13}\text{C}_5$  species of pyridine-formaldehyde complex (see Figures 3 and S1 for labelling).

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	v <sub>E</sub>	o-c
4	1	4	4		3	1	3	3	5502.125	0.000	5502.024	-0.001
4	1	4	3		3	1	3	2	5502.217	0.001	5502.115	-0.001
4	1	4	5		3	1	3	4	5502.300	0.001	5502.199	-0.001
4	0	4	3		3	0	3	2	5695.725	0.004	5695.584	-0.002
4	0	4	4		3	0	3	3	5695.772	-0.003	5695.640	-0.001
4	0	4	5		3	0	3	4	5695.833	0.000	5695.698	-0.001
4	1	3	3		3	1	2	2	5938.401	0.001	5938.267	0.002
4	1	3	4		3	1	2	3	5938.261	0.001	5938.126	0.001
4	1	3	5		3	1	2	4	5938.416	-0.002	5938.282	-0.002
5	1	5	5		4	1	4	4	6872.251	0.000	6872.128	0.002
5	1	5	4		4	1	4	3	6872.290	0.001	6872.164	-0.002
5	1	5	6		4	1	4	5	6872.350	-0.002	6872.231	0.003
5	0	5	4		4	0	4	3	7097.072	0.000	7096.904	0.000
5	0	5	5		4	0	4	4	7097.081	-0.001	7096.914	0.001
5	0	5	6		4	0	4	5	7097.137	0.000	7096.971	0.001

**Table S17.** Observed frequencies (MHz) for the  $^{13}\text{C}_6$  species of pyridine-formaldehyde complex (see Figures 3 and S1 for labelling).

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	v <sub>E</sub>	o-c
4	1	4	4		3	1	3	3	5536.725	-0.003	5536.623	0.001
4	1	4	3		3	1	3	2	5536.818	0.000	5536.713	-0.001
4	1	4	5		3	1	3	4	5536.900	-0.002	5536.797	0.000
4	0	4	3		3	0	3	2	5733.582	-0.003	5733.450	0.001
4	0	4	4		3	0	3	3	5733.640	0.001	5733.503	0.001
4	0	4	5		3	0	3	4	5733.698	0.000	5733.562	0.002
4	1	3	3		3	1	2	2	5982.058	-0.001	5981.919	-0.005
4	1	3	4		3	1	2	3	5981.919	0.000	5981.785	0.002
4	1	3	5		3	1	2	4	5982.079	0.002	5981.944	0.002
5	1	5	5		4	1	4	4	6915.238	0.005	6915.104	0.001
5	1	5	4		4	1	4	3	6915.275	0.002	6915.141	-0.001
5	1	5	6		4	1	4	5	6915.333	-0.002	6915.205	0.000
5	0	5	4		4	0	4	3	7143.262	0.000	7143.090	-0.003
5	0	5	5		4	0	4	4	7143.272	0.001	7143.102	0.001
5	0	5	6		4	0	4	5	7143.327	-0.001	7143.157	0.000

**Table S18.** Observed frequencies (MHz) for the  $^{13}\text{C}_{12}$  species of pyridine-formaldehyde complex (see Figures 3 and S1 for labelling).

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	v <sub>E</sub>	o-c
4	1	4	4		3	1	3	3	5502.036	0.000	5501.933	0.000
4	1	4	3		3	1	3	2	5502.127	0.000	5502.024	0.001
4	1	4	5		3	1	3	4	5502.209	-0.002	5502.107	-0.001
4	0	4	3		3	0	3	2	5694.108	0.000	5693.974	0.000
4	0	4	4		3	0	3	3	5694.162	-0.001	5694.028	-0.001
4	0	4	5		3	0	3	4	5694.220	-0.001	5694.086	-0.001
4	1	3	3		3	1	2	2	5934.010	0.002	5933.880	0.003
4	1	3	4		3	1	2	3	5933.867	-0.001	5933.735	-0.001
4	1	3	5		3	1	2	4	5934.026	0.000	5933.894	-0.001
5	1	5	5		4	1	4	4	6872.275	0.000	6872.148	0.001
5	1	5	4		4	1	4	3	6872.314	0.001	6872.184	-0.001
5	1	5	6		4	1	4	5	6872.377	0.001	6872.248	0.001
5	0	5	4		4	0	4	3	7095.621	-0.001	7095.457	0.001
5	0	5	5		4	0	4	4	7095.634	0.001	7095.467	0.001
5	0	5	6		4	0	4	5	7095.687	0.000	7095.521	-0.001

**Table S19.** Observed frequencies (MHz) for the  $^{13}\text{C}_{14}$  species of pyridine-formaldehyde complex (see Figures 3 and S1 for labelling).

J'	K' <sub>a</sub>	K' <sub>c</sub>	F'	←	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F''	v <sub>A</sub>	o-c	v <sub>E</sub>	o-c
4	1	4	4		3	1	3	3	5483.476	0.001	5483.376	-0.001
4	1	4	3		3	1	3	2	5483.566	0.000	5483.466	-0.002
4	1	4	5		3	1	3	4	5483.650	0.000	5483.553	0.001
4	0	4	3		3	0	3	2	5675.573	0.002	5675.437	-0.001
4	0	4	4		3	0	3	3	5675.624	-0.002	5675.492	0.000
4	0	4	5		3	0	3	4	5675.683	-0.001	5675.550	0.000
4	1	3	3		3	1	2	2	5916.199	0.003	5916.063	0.000
4	1	3	4		3	1	2	3	5916.056	-0.001	5915.921	-0.002
4	1	3	5		3	1	2	4	5916.213	-0.001	5916.079	-0.002
5	1	5	5		4	1	4	4	6848.998	-0.001	6848.876	-0.001
5	1	5	4		4	1	4	3	6849.040	0.002	6848.915	-0.001
5	1	5	6		4	1	4	5	6849.101	0.001	6848.978	-0.001
5	0	5	4		4	0	4	3	7072.136	-0.002	7071.972	0.001
5	0	5	5		4	0	4	4	7072.148	0.000	7071.983	0.003
5	0	5	6		4	0	4	5	7072.203	-0.001	7072.040	0.003
3	1	3	4		2	0	2	3	6837.651	0.000	6837.563	0.000