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Features of the C−H···N Weak Hydrogen Bond and Internal Dynamics in Pyridine–CHF_3

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The structural and energetic features of the C−H···N interaction and the internal dynamics of the pyridine–trifluoromethane molecular complex in its normal, ^{15}N and ^{13}C species are here reported. They have been obtained from analysis of the pure rotational spectra of the complex generated in a supersonic expansion.

Weak hydrogen bonds (WHB) are a major topic in hydrogen-bond research. The energies of these interactions lie within a few kJ mol^{-1} and approach those of van der Waals forces, but have the same directional properties of "classical" hydrogen bonds.[1] This behavior was recently shown for the C−H···O, C−H···F−C, C−H···S, and C−H···π linkages by investigating the rotational spectra of several hydrogen-bonded molecular complexes generated in supersonic jets.[2–4] With this technique, precise information on the energetics and on the structural and dynamical aspects of such interactions is obtained in an environment free from the intermolecular interactions that take place in condensed media.

Investigation of the rotational spectrum of benzene–trifluoromethane has shown that this complex is a symmetric top, with the two moieties held together through a C−H···π interaction,[4] and thus provided information on this kind of WHB. When replacing benzene with pyridine, two sites of high electronic density become available in the ring, so the two adducts shown in Figure 1 could be plausibly formed for the pyridine–trifluoromethane (Py–CHF_3) complex.

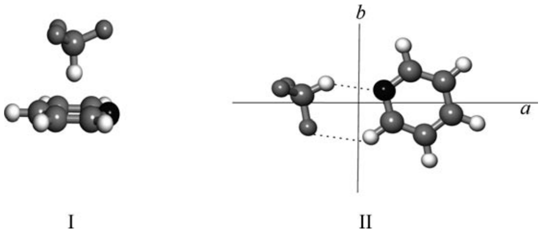

Figure 1. Plausible conformations of Py–CHF_3.

Conformation I resembles the shape of the complex formed between benzene and trifluoromethane, with a C−H···π linkage,[4] while species II is similar to the complexes that the three diazines form with water.[5] Before the search of the rotational spectrum was started, full geometry optimizations of the monomers and dimers were carried out at the MP2/6-311++G** level of theory by using the Gaussian 03 suite of programs.[6] All energies were corrected for basis set superposition error (BSSE) by using the counterpoise procedure.[7] The calculations suggest that form I is not a minimum, while for species II, we obtained the estimated values of the spectroscopic constants listed in the second column of Table 1. These values were used as a guide in the assignment of the spectrum of species II.

In Figure 2 we give the atom numbering, the principal axes system, and the parameters of the internal rotation of the CHF_3 group.

Following these predictions, two frequency scans of a few hundred MHz each were carried out in the region of the $J=$ 8–7 and 9–8 μ_a-type R bands. The corresponding $K_{-1}=0, 1$ transitions were easily assigned. Then, seven μ_a-type R bands, typical of a near-prolate top, evenly spaced by the $B+C$ value and with J in the range from 7 to 15 were measured on the whole, with K_{-1} ranging from 0 to 3. Most of

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Table 1. Ab initio (MP2/6-311++G**) and experimental spectroscopic constants for (^{14}N)Py–CHF$_3$ and (^{15}N)Py–CHF$_3$ adducts (S-reduction, I^r representation).

	(^{14}N)Py–CHF$_3$ ab initio	(^{14}N)Py–CHF$_3$ exptl.	(^{15}N)Py–CHF$_3$ exptl.
A [MHz]	3032.341	3054.63(2)[a]	3051.48(1)
B [MHz]	478.4126	478.7854(1)	478.345(3)
C [MHz]	445.8784	446.3809(1)	445.944(4)
D_J[b] [kHz]		0.11089[c]	0.11089(5)
D_{JK} [kHz]		4.402[c]	4.402(3)
d_1 [kHz]		−0.00391[c]	−0.00391(9)
d_2 [kHz]		0.0947[c]	0.0947(4)
χ_{aa} [MHz]	−4.07	−4.26(5)	
$\chi_{bb}-\chi_{cc}$ [MHz]	−2.11	−2.28(7)	
V_3 [kJ mol^{-1}]	0.517[d]	0.572[c]	0.572(3)
I_α [µÅ^2]		89.08[e]	89.08[e]
$\measuredangle(a,i)$ [°]		22.8[c]	22.8(8)
E_D [kJ mol^{-1}]	23.5[f]	14.9	
σ[g] [kHz]		4	2
N[h]		236	80

[a] Errors in parenthesis are expressed in units of the last digit. [b] The remaining quartic centrifugal distortion constant, D_K, is undetermined from the fit and has been fixed to zero. [c] Fixed to the value of the (^{15}N)Py–CHF$_3$ species. [d] The BSSE-corrected value is 0.336 kJ mol^{-1}. [e] Fixed to the value of I_a moment of inertia of CHF$_3$ (ref. [10]). [f] The BSSE-corrected value is 17.9 kJ mol^{-1}. [g] Standard deviation of the fit. [h] Number of fitted transitions.

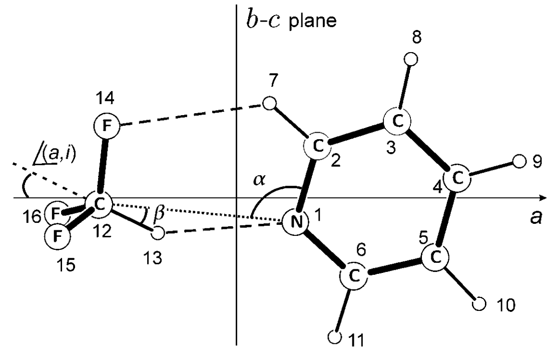

Figure 2. Configuration, principal axes (the b–c plane is perpendicular to the plane of the page), and atom numbering of the more stable conformer of Py–CHF$_3$.

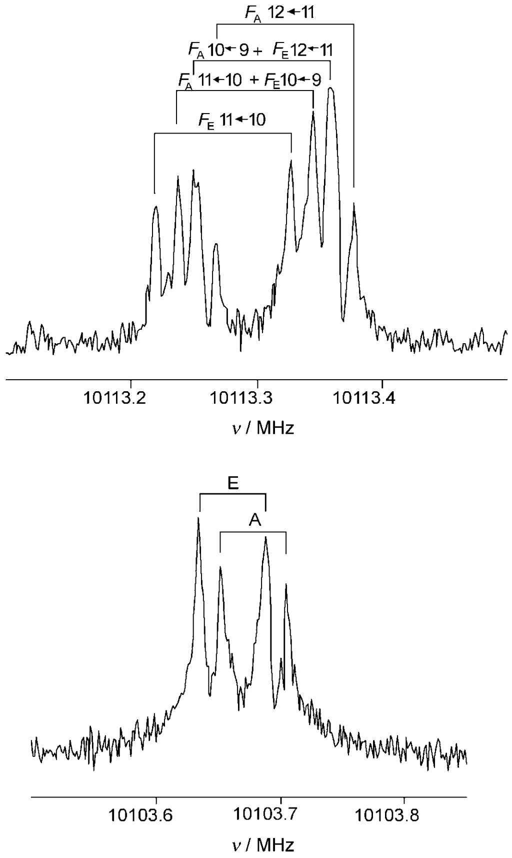

Figure 3. Recorded $11_{0,11}\leftarrow 10_{0,10}$ transitions of the (^{14}N)Py–CHF$_3$ (top) and (^{15}N)Py–CHF$_3$ (bottom) isotopologues. The ^{14}N hyperfine structure, the A and E internal rotation components, and the Doppler doubling are shown. F_A and F_E are the quadrupole coupling quantum numbers of the A and E states.

the rotational transitions were split into several components (from 1 to 6); this suggests that both the quadrupole coupling of the ^{14}N nucleus of pyridine and the hindered internal rotation of the CHF$_3$ group contribute to determine the pattern of the transitions. As shown in Figure 3, the splittings among the component lines are very small (in the range from 5 to 30 kHz), so it is difficult to discriminate the quadrupole from the internal rotation components. For this reason, we decided to study the spectrum of the (^{15}N)Py–CHF$_3$ isotopologue. The ^{15}N nucleus ($I=\frac{1}{2}$) does not generate any nuclear quadrupole coupling with the overall rotation. Thus, the transitions of this species exhibit only small internal rotation splittings, and the assignment of the corresponding A–E component lines was readily achieved. The experimental line frequencies were fitted with the XIAM[8] computer program, which takes into account the effects of the internal rotations within the combined axis method (CAM). In the CAM approach, a global fit to the absolute line positions of the A and E components is performed. A "rigid" limit set of rotational constants is determined, common to the two sublevels. Since Py–CHF$_3$ is a near symmetric top, the S reduction and I^r representation were chosen.[9]

The internal rotation parameters obtained for the ^{15}N species were subsequently used to assign the complicated pattern of the (^{14}N)Py–CHF$_3$ transitions. The fitted spectroscopic constants of both species are reported in Table 1 together with the ab initio values. Among these, $\measuredangle(a,i)$, the angle that the internal rotation axis forms with the a axis, was also determined from the fit. $\measuredangle(b,i)$ is the complement at 90°, and $\measuredangle(c,i)$ is 90° from the symmetry of the complex. The moment of inertia of the top, I_α, was fixed to the value of the I_a moment of inertia of the isolated CHF$_3$ molecule.[10] The E state transitions with $K_a=3$ were excluded from the fit because of their large residuals. Probably, as in the case of benzotrifluoride, a molecule with the same heavy internal rotor,[11] there is an interaction between the $K_a=3$ and $m=3$

levels (m is the torsional quantum number in the low barrier limit).

The much weaker spectra (~ 1 %) of the six singly substituted ^{13}C isotopologues were measured and assigned in natural abundance. The measured lines (reported in the Supporting Information) were fitted by keeping all the parameters fixed to the values of the parent species, except for the rotational constants, which are reported in Table 2.

Table 2. Rotational constants of the ^{13}C isotopologues of (^{15}N)Py–CHF_3. Centrifugal distortion and internal rotation constants have been fixed to the values of the ^{15}N species.

	A [MHz]	B [MHz]	C [MHz]	σ[a] [kHz]	N[b]
$^{13}C2$	3037.4(1)	477.5433(2)	444.9361(1)	3	12
$^{13}C3$	3020.81(6)	475.14939(6)	442.50435(5)	2	12
$^{13}C4$	3049.68(6)	472.32193(6)	440.65843(6)	4	14
$^{13}C5$	3033.18(8)	473.46023(9)	441.30125(8)	3	14
$^{13}C6$	3019.49(8)	476.6446(1)	443.77526(8)	3	16
$^{13}C12$	3051.5(1)	475.9841(1)	443.8795(1)	3	14

[a] Standard deviation of the fit. [b] Number of transitions of the fit.

The 24 ground-state rotational constants available were used to obtain the structural information. By applying Kraitchmann's equations,[12a] we calculated the substitution coordinates (r_s) of all the heavy atoms of the adduct lying in the symmetry plane, except those of fluorine. It was necessary to use (^{15}N)Py–CHF_3 as the parent species, because all the other isotopologues are obtained from it by isotopic substitution of a single atom. The r_s coordinates are shown in Table 3 together with the derived structural parameters. The estimated errors in r_s were calculated according to Costain's formula,[12b] $\delta z_i = 0.0012/|z_i|$ Å. The value of $|c|$ of the C12 atom results in a small imaginary number, probably due to the Coriolis effects of large-amplitude van der Waals vibrations being present in the dimer.

When comparing the ring r_s bond lengths to those of isolated pyridine[13] (N1–C2 = 1.3376(4), C2–C3 = 1.3938(5), and C3–C4 = 1.3916(4)) it could appear that the formation of the complex generates a sizable deformation of the ring, that is, an elongation of the C3–C4 and a shrinking of the C4–C5 bond lengths. However, such an effect is not confirmed in the ab initio structure, shown in Table 4. Actually, the intermolecular parameters in bold (the N···C distance, α, and β of Figure 2) were fitted (giving a partial r_0 structure) in order to reproduce the 24 available experimental rotational constants to within 0.5 MHz. The WHB parameters (H···N and F···H distances and C–H···N and C–H···F angles) were derived and are given at the bottom of the table.

Table 4. MP2/6-311++G** geometry of the heavy frame and of the H-bond parameters of Py–CHF_3.

Bond lengths [Å]		Valence angles [°]	
N1–C2	1.346	N1–C2–C3	123.6
C2–C3	1.398	C2–C3–C4	118.7
C3–C4	1.397	C3–C4–C5	118.4
C4–C5	1.397	C4–C5–C6	118.7
C5–C6	1.398	C5–C6–N1	123.6
C6–N1	1.345	C6–N1–C2	117.1
C12–N1	**3.287(1)**[a]	α	**101.1(2)**
		β	**22.2(1)**
Derived WHB parameters			
N···H13	2.317(1)	C12–H13–N	147.6(2)
F14···N7	2.700(7)	C2–H7–F14	129.5(2)

[a] Error in parentheses in units of the last digit. The ab initio values of the three fitted parameters (in bold) are 3.289 Å, 100.4° and 19.7°, respectively.

Table 3. The r_s coordinates of the seven singly substituted atoms in the principal axes system of (^{15}N)Py–CHF_3, and the corresponding r_s structural parameters.

	r_s coordinates		r_s structural parameters			
	$\lvert a\rvert$ [Å]	$\lvert b\rvert$ [Å]	Bond lengths		Valence angles	
N1	0.973(4)[a]	0.411(4)	N1–C2	1.344(4)	N1–C2–C3	123.7(4)
C2	1.350(3)	0.878(4)	C2–C3	1.392(3)	C2–C3–C4	117.8(5)
C3	2.676(1)	1.304(2)	C3–C4	1.411(5)	C3–C4–C5	118.8(7)
C4	3.683(1)	0.316(7)	C4–C5	1.374(7)	C4–C5–C6	119.0(7)
C5	3.312(1)	1.008(3)	C5–C6	1.395(2)	C5–C6–N1	123.4(3)
C6	1.954(2)	1.330(2)	C6–N1	1.344(2)	C6–N1–C2	117.2(4)
C12	2.303(2)	0.030i	C12–N1	3.30(1)	C12–N1–C2	99(1)

[a] Error in parentheses in units of the last digit.

The WHB H···N distance is somehow the "new" parameter determined by rotational spectroscopy, while the WHB F···H distance is in line with those observed for the complexes oxirane–CHF_3, oxirane–CH_2F_2, dimethyl ether–difluoroethene and dimethyl ether–trifluoroethene.[2,3]

Looking at the geometry and symmetry of the complex, it can be seen that the stretching motion leading to its dissociation is almost parallel to the a axis. This allows us to estimate the stretching force constant (k_s) by using the approximated equation:[14]

$$k_s = \frac{16\pi^4(\mu_A R_{CM})^2[4B_A^4 + 4C_A^4 - (B_A - C_A)^2(B_A + C_A)^2]}{hD_J} \qquad (1)$$

where the suffix A is for "Adduct" and μ_A, R_{CM}, and D_J are the reduced mass, the distance between the centers of mass, and the first-order centrifugal distortion constant, respectively. From Equation (1), the value $k_s = 7.3\ N\,m^{-1}$, corresponding to a harmonic stretching frequency of $58\ cm^{-1}$, was obtained; the value of R_{CM}, calculated from our geometry, is 4.95 Å; while the dissociation energy (E_D) was evaluated to be $14.9\ kJ\,mol^{-1}$ by assuming a Lennard–Jones potential function, according to:[14] $E_D = 1/72\,k_s R_{CM}^2$. E_D is in good agreement with the ab initio value, once the BSSE corrections have been included (see Table 1). As expected, the C–H···N interaction is stronger than the C–H···π linkage observed in benzene–CHF_3 ($\Delta E_D = 8.6\ kJ\,mol^{-1}$). Its value is about the half of that observed for classical (e.g., O–H···N or O–H···O) hydrogen bonds. In addition, we can estimate the strength of the "secondary" interaction C−H···F. In fact, the V_3 barrier to internal rotation of the CHF_3 moiety (0.57 kJ mol^{-1}) corresponds, in a first approximation, to the energy of such a WHB. In this case, the experimental result is in better agreement with the ab initio value before BSSE corrections.

This investigation supplies for the first time the rotationally determined WHB H···N distance in molecular complexes, and completes the structural and energetic characterization of WHB interactions with rotational spectroscopy, after those of the C−H···O, C−H···F−C, C−H···S and C−H···π linkages.[2–4]

Experimental Section

Commercial samples of pyridine, ^{15}N-pyridine (98 % enriched), and CHF_3 (Aldrich) were used without further purification. The rotational spectra in the 6–18.5 GHz frequency region were measured on a COBRA-type[15] pulsed supersonic-jet Fourier-transform microwave (FTMW) spectrometer,[16] described elsewhere,[17] recently updated with the FTMW++ set of programs.[18] A gas mixture of 1 % of CHF_3 in Ne at a total pressure of ca. 4 bar was streamed over liquid pyridine at room temperature, and expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry–Pérot cavity. Each rotational transition displays a Doppler splitting that originates from the supersonic jet's expanding coaxially along the resonator axes. The rest frequency was calculated as the arithmetic mean of the frequencies of the two Doppler components. The estimated accuracy of the frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

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Keywords: hydrogen bonds · internal dynamics · molecular complexes · pulsed jets · rotational spectroscopy

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