Molecular Complexes

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The C–H···π Hydrogen Bond in the Benzene–Trifluoromethane Adduct: A Rotational Study[**]

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Herein, we report the structural and energetic features of the C–H···π interaction obtained from the analysis of the pure rotational spectra of the benzene–trifluoromethane molecular complex in its normal and ^{13}C-benzene species. The complexes were generated in a supersonic jet and characterized by Fourier transform microwave spectroscopy (FTMW).

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, and CH···S WHB interactions from investigations of the rotational spectra of several hydrogen-bonded molecular complexes generated in supersonic jets.[2–3] With this technique, precise information on the energetics and structural and dynamical aspects of such interactions is obtained in an environment free of the intermolecular interactions that take place in condensed media.

A special type of weak hydrogen bond is that in which the proton acceptor is a π system, its role as Lewis base being well established after the pioneering work of Pimentel and co-workers.[4] In recent years, there has been an increasing interest in C–H···π interactions.[5] The C–H group can display a wide range of polarities, and C–H···π interactions have been suggested to play important roles in many aspects of organic, biological, and supramolecular chemistry.[5] There is, however, a small amount of rotational information concerning weak C–H···π linkages.[6–8]

Benzene is the prototype of an aromatic π-system proton acceptor, and, indeed, O–H···π_{arom} and N–H···π_{arom} interactions have been characterized through rotational spectroscopy for C_6H_6–H_2O[9] and C_6H_6–NH_3.[10] Trifluoromethane (fluoroform, CHF_3) represents the prototype of a weak proton donor owing to the polarized character of its aliphatic C–H bond, which lies adjacent to three electron-withdrawing fluorine atoms. Within this role, it has been used as a partner to different proton-acceptor molecules to study C–H···O, C–H···S, and C–H···F weak hydrogen bonds.[3] Herein, we investigated the rotational spectrum of the benzene–trifluoromethane (C_6H_6–HCF_3) complex, which is probably an ideal model to analyze the energetics and structure of the C–H···π interaction.

The complex C_6H_6–HCF_3 was generated in a supersonic expansion, and its rotational spectrum was characterized by FTMW spectroscopy (see Experimental Section). After scans over a wide frequency range, six evenly spaced bands with the typical features of a symmetric top were observed, consistent with the C_{3v} configuration of the complex depicted in Figure 1. In Figure 2 we report the $J=8\leftarrow7$ transition, which, at high resolution, shows the complex pattern that arises from the practically free internal rotation of CHF_3 with respect to C_6H_6. Such a motion has been observed in several molecules[11] and complexes[12] with two internal symmetric rotors. In the present case, considering the C_6H_6 moiety as the framework, the internal rotation state of the complex is specified by the quantum number m, which gives the projection of the angular momentum of the CHF_3 unit on

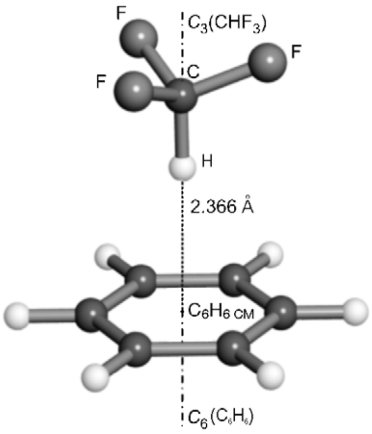

Figure 1. Drawing of the benzene–trifluoromethane adduct showing the collinearity of the symmetry axes of the two moieties and the distance $r(H\cdots C_6H_{6CM})$. CM = center of mass.

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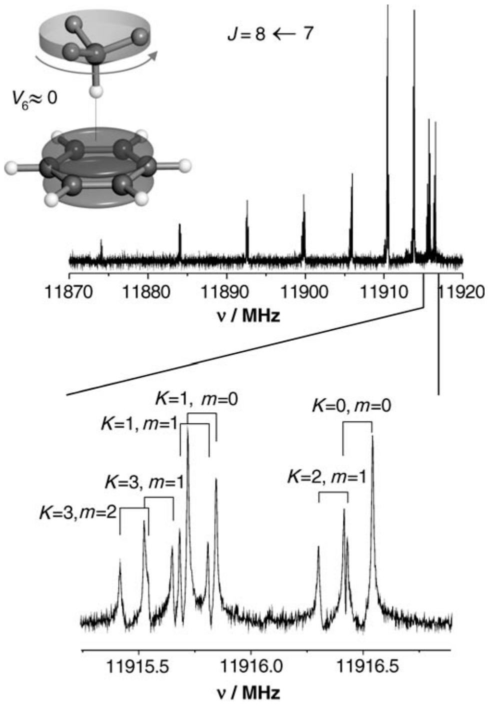

Figure 2. The $J+1 \leftarrow J = 8 \leftarrow 7$ band of the benzene–trifluoromethane complex (upper trace). The high-resolution details (lower trace) show the complex patterns due to free internal rotation. Each rotational transition, split by the Doppler effect (⌈ ⌉), is labeled with the quantum numbers *K* and *m*.

Table 1: Spectroscopic constants of the two isotopomers of C_6H_6–HCF_3.

Parameter	C_6H_6–HCF_3	$[1\text{-}^{13}C]C_6H_6$–HCF_3
A' [MHz]	–	2837(6)[a]
B [MHz]	744.840122(65)	741.33150(6)
C [MHz]		739.19544(6)
D_J [kHz]	0.46995(54)	0.4640(4)
D_{JK} [kHz]	42.3923(68)	41.792(8)
D_{Jm} [kHz]	166.820(18)	–
D_{JKm} [kHz]	−164.702(18)[b]	–
H_{JK} [Hz]	1.775(55)	1.49(6)
H_{KJ} [Hz]	−1.00(15)	–
H_{Jm} [Hz]	7.27(14)	–
H_{mJ} [Hz]	−37.17(83)	–
H_{JKm} [Hz]	7.48(12)[b]	–
$L_{JK^3m^3}$ [Hz]	1.96(38)[b]	–
σ[c] [kHz]	1.9	0.9
N[d]	125	34

[a] Standard errors in parentheses are given in units of the last digit. [b] The sign given for these constants is arbitrary. The sign given here corresponds to the choice of the sign of *m* given in Table 1 of frequencies (see Supporting Information). [c] Root-mean-square deviation of the fit. [d] Number of fitted transitions.

the symmetry axis of the complex. In this way, the rotational transitions are uniquely labeled by J, $|K|$, and $\pm m$.[11,12] The observed frequencies were interpreted using the expression shown in Equation (1).

$$\begin{aligned}\nu = {} & 2(J+1)[B - D_{JK}K^2 + H_{KJ}K^4 - D_{Jm}m^2 + H_{mJ}m^4 - D_{JKm}Km \\ & + L_{JK^3m^3}K^3m^3] - 4(J+1)^3[D_J - H_{JK}K^2 - H_{Jm}m^2 - H_{JKm}Km]\end{aligned} \tag{1}$$

D_{JK}, D_{Jm}, and D_{JKm} are quartic centrifugal distortion constants. Higher order constants such as H_{JK}, H_{KJ}, H_{Jm}, H_{mJ}, H_{JKm}, or $L_{JK^3m^3}$ were found necessary to fit the data, given the extreme flexibility of the adduct. The parameters determined from the least-squares fit of a total of 125 lines are provided in Table 1.

As the benzene ring contains six equivalent carbon atoms, the spectrum of the $[1\text{-}^{13}C]C_6H_6$ species in natural abundance is expected to display an intensity of 6% of that of the most abundant species and the features of a slightly asymmetric top because the asymmetric isotopic substitution breaks down the C_{3v} symmetry of the complex. In addition, as typical of molecular systems with free internal rotation[13] in the ground state ($m = 0$), the internal rotor (the CHF_3 subunit in our case) does not rotate. Consequently, the moment of inertia I_a does not take into account its mass contributions. This means that the value of the rotational constant A' should be coincident with the value of the rotational constant $C =$ 2813.8 MHz calculated for bare mono-^{13}C-substituted benzene.[14,15] Following this model, we could identify 34 transitions of the $m = 0$ spectrum of the $[1\text{-}^{13}C]C_6H_6$–HCF_3 asymmetric-top species. These were fitted to the I^r representation of Watson's "*S*"-reduced Hamiltonian,[16] producing the spectroscopic constants reported in the second column of Table 1. The agreement between the rotational and centrifugal distortion constants for the parent and $[1\text{-}^{13}C]C_6H_6$–HCF_3 species supports the assignments. (All measured rotational frequencies are available in the Supporting Information.)

The experimental evidence that the normal species is a symmetric top and that the $[1\text{-}^{13}C]C_6H_6$–HCF_3 species is an asymmetric top leaves little doubt about the conformation of the complex shown in Figure 1. By assuming that the structures of the monomers[14,15,17] are not altered upon formation of the complex, the distances between the hydrogen atom of CHF_3 and the center of mass (CM) of benzene, $r(H\cdots C_6H_{6\,CM}) = 2.366(2)$ Å, and that between the two centers of mass, $r_{CM} = 3.8286$ Å, were calculated from the rotational constants.

The experimental evidence of an almost-free internal rotation are consistent with ab initio computations[18] at the MP2/6-311++G(d,p) level, including BSSE CP (basis-set superposition error counterpoise) corrections, which predict a V_6 barrier of less than 0.2 cm^{-1}.

Six low-energy vibrational modes take origin from the formation of the adduct, as the three translational and the three rotational degrees of freedom of one subunit disappear. We have already seen the effects on the spectra of one of these motions, the internal rotation of the CHF_3 subunit. Also, the stretching between the centers of mass of the two constituent molecules can be, in a first approximation, separated from the remaining vibrational modes. For symmetric-top complexes, such as C_6H_6–HCF_3, the stretching-force constant (k_s) can be estimated by approximating the complex to a molecule made of two rigid parts. This can be done by using the so-called pseudodiatomic approximation, expressed by Equation (2).[19]

$$k_s = 128\,\pi^4\,(\mu\, r_{CM})^2\, B^4/(h\, D_J) \qquad (2)$$

where μ, r_{CM}, and D_J are the reduced mass, the distance between the centers of mass, and the first-order centrifugal distortion constant, respectively. Contributions to the D_J parameter from the free internal rotation of the CHF_3 group were calculated to be zero as a consequence of the collinearity between the principal axis *a* of the complex and the internal rotation axis.[20] By using $r_{CM} = 3.8286$ Å in Equation (2), we obtained $k_s = 6.8\ N\,m^{-1}$ and $\nu_{str} = 56\ cm^{-1}$. The dissociation energy (E_D) was evaluated to be 8.4 kJ mol^{-1} by assuming a Lennard-Jones potential function, according to the approximation shown as Equation (3).[21]

$$E_D = 1/72\, k_s\, r_{CM}^2 \qquad (3)$$

The value of 8.4 kJ mol^{-1} is in reasonable agreement with the MP2/6-311++G(d,p) ab initio CP-corrected dissociation energy of 12.6 kJ mol^{-1} calculated in this work and with that calculated previously for the C–H···π-bonded form of C_6H_5F–HCF_3 ($E_D = 8.6$ kJ mol^{-1}).[22]

Structural data obtained from the rotational spectra, such as distances and dissociation energies, can be used to infer the nature of the WHB interactions. In the case of C–H···π interactions, no atom–atom distances are given but we can take $r(H\cdots C_6H_{6\,CM})$ as the C–H···π hydrogen-bond distance. Its value of 2.366(2) Å in C_6H_6–HCF_3 is remarkably shorter than those of 2.78 Å and 2.74 Å determined for the acetylene dimer[6] and the acetylene–ethylene complex,[7] respectively. The dissociation energy (8.4 kJ mol^{-1}) of the C_6H_6–HCF_3 complex is higher than those observed for the acetylene dimer (5.6 kJ mol^{-1})[6] and ethylene–acetylene (4.1 kJ mol^{-1})[7]. Both structural and energetic data support that the C–H···π_{arom} WHB bonds to aromatic rings are stronger than C–H···$\pi_{\equiv}$ or C–H···$\pi_{=}$ WHB interactions to triple or double bonds, respectively.

Let us discuss the C–H···C hydrogen bonds. The C_6H_6–HCF_3 complex could be considered as formed by a hexafurcated C–H···C_6 hydrogen bond. From the distance $r(H\cdots C_6H_{6\,CM}) = 2.366$ Å and the structure of benzene, the atom–atom distance $r_{H\cdots C} = 2.738$ Å is obtained which is similar to the C–H···O, C–H···S, and C–H···F–C WHB distances.[2,3] The dissociation energy for C_6H_6–HCF_3 is also of the same order of magnitude as determined for complexes formed by a combination of those bonds.[2,3] The individual energies of the C–H···O, C–H···S, or C–H···F–C interactions, which are calculated to be approximately 2.0 kJ mol^{-1},[2,3] are lower than that of the C–H···π_{arom} linkage. However, if this energy is interpreted as a sum of contributions from six C–H···C WHB interactions, it appears that each C–H···C contact (1.4 kJ mol^{-1}) would be weaker than each of the C–H···O, C–H···S, or C–H···F–C interactions.

The most interesting results of our investigation are:

1) The unrivalled resolving power and precision of molecular beam (MB)-FTMW spectroscopy allowed the detailed analysis of the spectrum of C_6H_6–HCF_3 and the determination of accurate spectroscopic parameters which supplied important chemical information, such as the structure or dissociation energy.
2) Here we show that in the complex C_6H_6–HCF_3, the CHF_3 moiety undergoes an almost fully free rotation.
3) The structural and energetic data obtained in this work on C_6H_6–HCF_3 reveal that the C–H···π_{arom} WHB bonds to aromatic rings are stronger than C–H···$\pi_{\equiv}$ or C-H···$\pi_{=}$ WHB interactions to triple or double bonds, respectively.
4) We note that while in previous WHB-linked adducts, a cooperative effect of some WHBs was required to stabilize them, for C_6H_6–HCF_3 a single C–H···π_{arom} bridge reaches the stability of maybe three or four C–H···O or C–H···F–C weak interactions. One could consider that the energy of the interaction between the benzene crown π system with the CHF_3 hydrogen atom is equivalent in magnitude to the sum of three or four of these weak interactions.

Experimental Section

Commercial samples of benzene and CHF_3 (Aldrich) were used without further purification. The spectrum of the monosubstituted [1-^{13}C]C_6H_6–HCF_3 isotopic species was measured in natural abundance.

The MB-FTMW spectrum in the 5–14 GHz frequency region was measured by using a molecular beam Fourier transform microwave spectrometer, as described previously.[23] A gas mixture of 2 % of C_6H_6 and 2 % HCF_3 in He at a total pressure of 1.5 bar was expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.8 mm) into the Fabry-Pérot cavity. The frequencies were determined after Fourier transformation of the 8k data points time-domain signal, recorded at 100-ns intervals. Each rotational transition is split by a Doppler effect owing to the coaxial arrangement of the supersonic jet and resonator axes. The rest frequency is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

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