Weak C−H⋯O and C−H⋯F−C Hydrogen Bonds in the Oxirane−Trifluoromethane Dimer

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Abstract: The oxirane−trifluoromethane dimer generated in a supersonic expansion has been characterized by Fourier transform microwave spectroscopy. The rotational spectra of the parent species and of its two ^{13}C isotopomers in combination with ab initio calculations have been used to establish a C_s geometry for the dimer with the two monomers bound by one C−H⋯O and two C−H⋯F−C hydrogen bonds. An overall bonding energy of about 6.7 kJ/mol has been derived from the centrifugal distortion analysis. The lengths of the C−H⋯O and C−H⋯F hydrogen bonds, $r(O⋯H)$ and $r(F⋯H)$, are 2.37 and 2.68 Å, respectively. The C−H⋯F−C interactions give rise to the HCF_3 internal rotation motion barrier of 0.55(1) kJ/mol, which causes the A−E splittings observed in the rotational spectra. The analysis of the structural and energetic features of the C−H⋯O and C−H⋯F−C interactions allows us to classify them as weak hydrogen bonds. Ab initio calculations predict these weak interactions to produce blue shifts in the C−H vibrational frequencies and shortenings of the C−H lengths.

Introduction

So much scientific interest has been dedicated during past years to the weak hydrogen bond (WHB), a noncovalent interaction which manifests itself in myriad ways in structural chemistry and biology, that this topic deserved recently the publication of a book.[1] Several weak proton donors and proton acceptors, whose interaction energies are within a few kJ/mol, have been considered and classified there. The C−H⋯O, C−H⋯N, and C−H⋯π interactions appear to be the most important ones in solvation processes and in biological and supramolecular chemistry; the C−H⋯halogen interactions are of importance in atmospheric chemistry.

There have been some disputes on the classification of the WHB, either as a real H-bond or as a van der Waals interaction.[2−4] Several recent papers agree in considering the WHB as a "true" H-bond.[3−7] An alternative nomenclature for WHB is "improper blue shifted H-bond",[8−10] because, in contrast with "normal H-bonds", an increase of the frequency of the C−H stretching (blue shift) upon formation of the H-bond

is generally observed. Because of this inversion in the frequency shift, WHB has also been called, erroneously, an anti-hydrogen bond.[11−13] Several authors view conventional and "improper H-bonds" as similar in nature, being red or blue shifted as a consequence of the balance between opposite factors.[4,7,14]

The experimental information on WHB interactions used in ref 1, mainly from solid state or solution investigations, is contaminated from other intermolecular interactions which take place in condensed phases. The gas-phase investigations are free from such effects and can give more details on specific or local interactions.[15] In the case of rotationally resolved experiments, the obtained data are generally so reliable and precise that they are used as benchmarks to test various theoretical approaches. Only a few such high-resolution investigations are available on WHB. The three C−H⋯F−C WHB interactions of the difluoromethane dimer have been characterized from its pure rotational spectrum.[16] Each C−H⋯F−C interaction was estimated to have an energy of about 2.2 kJ/mol with a blue shift of the C−H stretching in the range 13−21 cm^{-1}. Similar detailed information has been obtained on the three C−H⋯O WHB interactions of dimethyl ether dimer.[17] The effects of such interactions on the conformations of the two dimers have been outlined.[16,17]

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Trifluoromethane (HCF_3) and oxirane (C_2H_4O) can be thought as having a double nature as WHB proton donors and acceptors. The $C-H\cdots O$ interaction in the dimer of HCF_3 and C_2H_4O has been studied through IR investigation of their 1:1 adduct in liquid krypton.[9] This work was mainly dedicated to observing the blue shift of the $C-H$ stretching of HCF_3 upon formation of the $C-H\cdots O$ WHB. Ab initio calculations[12,18] on this complex were done with the same purpose. In these works, no attention was given to the $C-H\cdots F-C$ interactions. This has been pointed out only recently,[14] at the time we were writing the present paper. Because no gas-phase experimental information on the $C_2H_4O\cdots HCF_3$ adduct was available, we decided to generate it in the supersonic jet of a molecular beam Fourier transform microwave (MB-FTMW) experiment. This has allowed us to characterize its conformation and therefore to obtain detailed structural information and energetics on the $C-H\cdots F-C$ and $C-H\cdots O$ interactions from the rotational spectrum. These results in conjunction with the relatively high level ab initio calculations reported here constitute significant information for a better understanding of the relative importance of these two weak intermolecular interactions. It will be shown that these interactions are WHB in nature.

Experimental Section

Commercial samples of C_2H_4O and HCF_3 (Aldrich) have been used without further purification. The spectra of the isotopic ^{13}C species have been measured in natural abundance.

The MB-FTMW spectrum in the 6−18.5 GHz frequency region was measured using a molecular beam Fourier transform microwave spectrometer described elsewhere.[19] A gas mixture of 2% of C_2H_4O 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 with 100 ns sample intervals. Each rotational transition is split by the Doppler effect due 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.

Rotational Spectra

The FTMW spectra of $C_2H_4O\cdots HCF_3$ were predicted by using the rotational constants obtained from model calculations of the plausible structures for the complex.[12] After wide frequency range scans, the spectrum of only one rotamer was detected and assigned in the supersonic expansion. Five lines (K_{-1} from 0 to 2) of the μ_a-R band with $J = 5 \leftarrow 4$ were assigned in the first stage. Five more μ_a-R bands with J_{upper} in the range 3−8 were then measured. Finally, we could measure five weaker μ_c-R lines. No μ_b-type transitions were observed. Each rotational transition was split into two A,E components due to the internal rotation of the trifluoromethyl group. The analysis of the A−E splittings will be considered later. The A component lines have been fitted within the I^r representation of Watson's "A" reduced Hamiltonian,[20] producing the spec-

Table 1. Spectroscopic Constants for Three Isotopomers of $C_2H_4O\cdots HCF_3$

	$C_2H_4O\cdots HCF_3$	$^{13}CCH_4O\cdots HCF_3$	$C_2H_4O\cdots H^{13}CF_3$
A/MHz	5264.8472(47)[a]	5233.71(35)	5262.63(88)
B/MHz	1177.6737(20)	1161.4756(37)	1173.7663(11)
C/MHz	1096.6055(19)	1081.3947(35)	1093.29738(91)
P_b/u Å^2	63.85777(81)[b]	64.3921(47)	63.8609(84)[b]
Δ_J/kHz	1.4047(68)	1.3891(81)	1.3922(98)
Δ_{JK}/kHz	265.49(33)	265.154(98)	263.98(62)
Δ_K/kHz	−288.5(12)	[−288.5][c]	[−288.5]
δ_J/kHz	0.1559(41)	0.1603(36)	0.1607(73)
δ_K/kHz	133.15(88)	135.9(17)	[133.15]
H_{JJK}/kHz	0.0506(23)	[0.0506]	[0.0506]
H_{JKK}/kHz	0.137(67)	[0.137]	[0.137]
σ^d/kHz	6.7	4.2	3.2
N^e	30	24	16

[a] Standard error in parentheses in units of the last digits. [b] $P_b = (I_a - I_b + I_c)/2 = \sum_i m_i b_i^2$. Conversion factor 505 379.1 MHz u Å^2. [c] Parameters in square brackets were kept fixed in the fit. [d] rms deviation of the fit. [e] Number of fitted transitions.
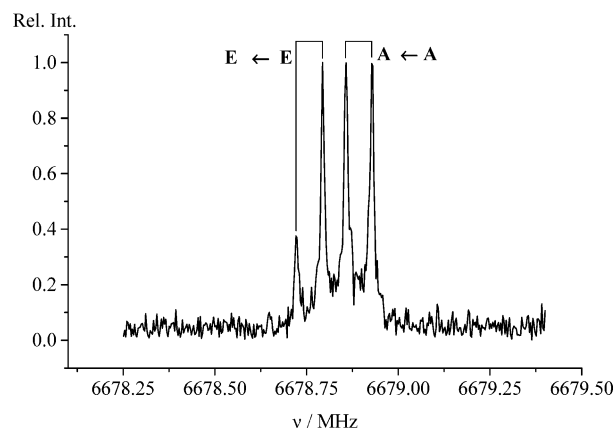

Figure 1. Internal rotation of the HCF_3 group: A,E component lines of the $3_{1,3}$-$2_{1,2}$ transition of the $C_2H_4O\cdots H^{13}CF_3$ isotopic species in natural abundance. In addition, each component is split by the Doppler effect.

troscopic constants of Table 1. Besides rotational and quartic centrifugal distortion constants, some sextic centrifugal distortion parameters have been determined for the normal species. The high values of the centrifugal distortion parameters are related to the motions of the two monomers with respect to each other, as we will discuss later.

Following the same procedure, the very weak μ_a-type spectra of the monosubstituted ^{13}C isotopomers in natural abundance were assigned and measured. The spectrum of only one isotopomer of the $^{13}CCH_4O\cdots HCF_3$ species corresponding to ^{13}C substitution within the oxirane subunit was observed. Their lines were 2 times more intense than those corresponding to the $C_2H_6O\cdots H^{13}CF_3$ species, in agreement with the natural abundances of 2% and 1%, respectively. These observations indicate that the two oxirane carbon atoms are at equivalent positions in the adduct. As it occurs for the parent species, each transition line was split into the two internal rotation components A,E shown in Figure 1. The rotational spectrum was analyzed in the same way as that described for the parent species, and the rotational parameters are also collected in Table 1. The measured rotational frequencies for all isotopomers are available as Supporting Information.

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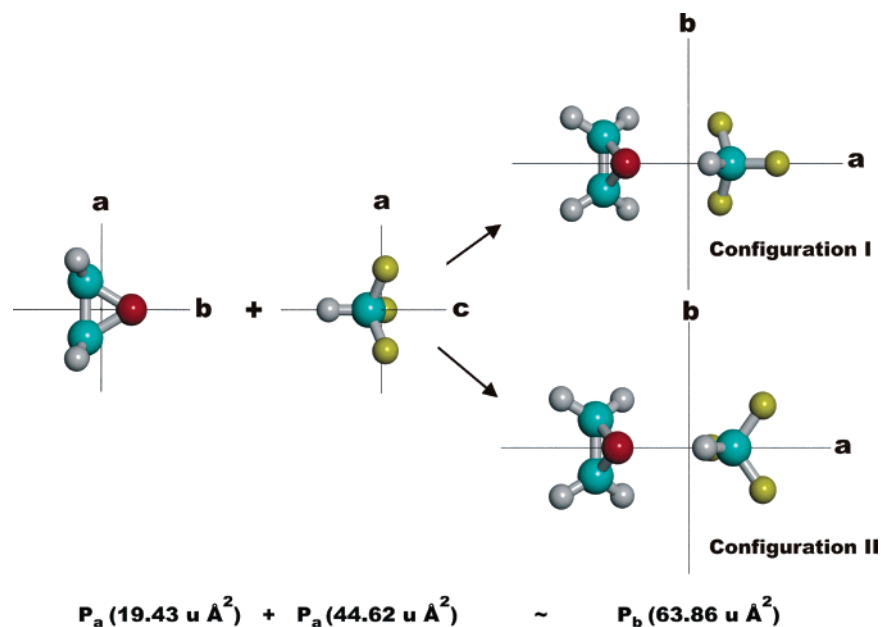
$$P_a (19.43 \text{ u Å}^2) \quad + \quad P_a (44.62 \text{ u Å}^2) \quad \sim \quad P_b (63.86 \text{ u Å}^2)$$

Figure 2. The sum of the experimental planar moments $P_a = \sum_i m_i a_i^2$ of the isolated monomers HCF$_3$[22] and oxirane[21] reproduces the planar moment $P_b = \sum_i m_i b_i^2$ of the complex oxirane$\cdots$HCF$_3$ for configuration I or II.

Conformation and Structure

The spectroscopic constants of Table 1 provide the experimental information needed to establish unambiguously the symmetry of the heterodimer, based on the following arguments: (i) The value of the planar moment P_b for the complex is virtually unchanged upon the ^{13}C isotopic substitution on the carbon of the HCF$_3$ subunit, which demonstrates that this atom lies in the *ac* plane of the complex. (ii) The experimental observation of two equivalent monosubstituted ^{13}C species in the C$_2$H$_4$O subunit reveals that the *ac* inertial plane is also a symmetry plane for the complex. (iii) The P_b values of Table 1 for the parent, C$_2$H$_4$O$\cdots$HCF$_3$, and the C$_2$H$_4$O$\cdots$H[13]CF$_3$ isotopic species are consistent with the value 64.05 u Å^2 resulting from the sum of the P_a's of isolated C$_2$H$_4$O[21] and HCF$_3$.[22] Two possible configurations for the complex (I and II, illustrated in Figure 2) arise. (iv) The failure to observe μ_b-type transitions is a further indication that *ac* is a plane of symmetry. The above leads to the conclusion that C$_2$H$_4$O$\cdots$HCF$_3$ must have C_s symmetry given that the *ac* inertial plane is the symmetry plane.

The experimental rotational constants are consistent with those predicted for the C_s configurations I and II of Figure 3, both of them presenting a C$-$H$\cdots$O hydrogen bond. Configuration I shows two C$-$H$\cdots$F$-$C interactions, while configuration II shows one bifurcated C$-$H$\cdots$F$\cdots$H$-$C disposition. Both forms may interconvert by a 60° rotation of HCF$_3$ around its C_3 symmetry axis without changing the values of the rotational constants. Unfortunately, no fluorine isotopic substitution is possible to discriminate between the two plausible forms, so that, although chemical intuition suggests structure I as the most stable, it is not possible to state which of the two structures is the most stable from the available experimental data. Ab initio computations at the MP2/6-311+G(d, p) and MP2/6-311++G-(2df, 2p) levels[23] established that form I corresponds to the global minimum while II corresponds to a transition structure, with energy differences of 0.72 and 0.90 kJ/mol, respectively.
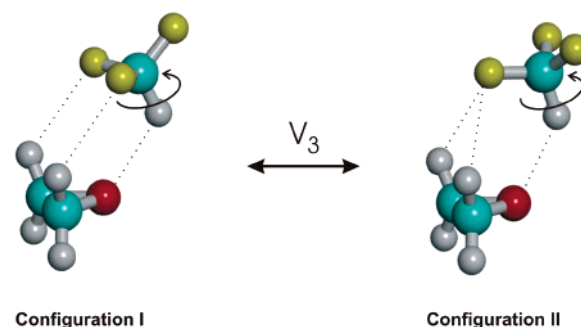
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Figure 3. The two structures of C$_2$H$_4$O$\cdots$HCF$_3$ compatible with the spectroscopic parameters determined in this work. We show here that configuration I, with one C$-$H$\cdots$O and two C$-$H$\cdots$F$-$C interactions, corresponds to the global minima. A 60° rotation around the fluoroform C$-$H bond converts the molecule to configuration II, with one C$-$H$\cdots$O and one bifurcated C$-$H$\cdots$F$-$C interaction. This form is located at the maximum of the HCF$_3$ internal rotation V_3 barrier, representing a transition state for the interconformational pathway.

From the available rotational constants of Table 1, the positions of the carbon atoms with respect to the center of mass were obtained using the substitution method of Kraitchmann.[24] The corresponding r_s distances are collected in Table 2. The position of the two subunits with respect to each other is determined by the H-bond parameters φ, θ, and $r_{O\cdots H}$ shown in Figure 4. These were calculated by fitting the nine available rotational constants. The determined r_0 values, along with other derived structural parameters, are also shown in Table 2. It was assumed that the structures of C$_2$H$_4$O[21] and CF$_3$H[22] are

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Table 2. Structural H-Bond Parameters for $C_2H_4O \cdots HCF_3$ (See Figure 4)

	r_0		r_s
$r_{O \cdots H}$/Å	2.42(2)[a]	r_{C-C}/Å[c]	1.478(6)
$r_{F \cdots H}$/Å	2.74(1)[b]	$r_{C \cdots C}$/Å[d]	3.720(1)
φ/deg	126(1)		
θ/deg	118.4(2)		
$\angle(a, C-H)$	56° [b]		

[a] Standard error in parentheses in units of the last digits. [b] Derived parameters. [c] Oxirane r_s C−C bond length in the complex. [d] r_s C⋯C distance between the carbon atoms of C_2H_4O and HCF_3.
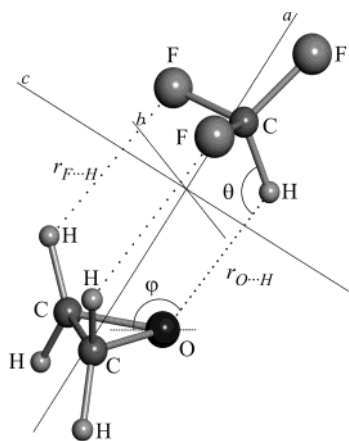
Figure 4. Configuration and structural parameters of the global minimum of $C_2H_4O \cdots HCF_3$.

Table 3. MP2/6-311++G(2df,2p) Values of the H-Bond Parameters, Rotational Constants, Electric Dipole Moment Components, and BSSE Corrected Dissociation Energy of $C_2H_4O \cdots HCF_3$

H-bond parameters		spectroscopic parameters	
$r_{O \cdots H}$/Å	2.367	A/MHz	5362
$r_{F \cdots H}$/Å	2.683	B/MHz	1219
φ/deg	128.6	C/MHz	1129
θ/deg	116.5	μ_a/D	2.20
$\angle(a, C-H)$	59.7°	μ_b/D	0
E_d/kJ mol^{-1}	15.7[a]	μ_c/D	0.48

[a] The E_d value without BSSE corrections is 21.6 kJ mol^{-1}.

unperturbed upon formation of the complex as has been experimentally proven.[25,26] This assumption is supported in this case by the concordance of the oxirane r_s C−C bond length in the complex (see Table 2) with that of the isolated molecule of 1.465(2) Å.[21]

The results of the ab initio MP2/6-311++G(2df, 2p) calculations are presented in Table 3. The predicted rotational constants and structural parameters are in excellent agreement with the experimental values given in Tables 1 and 2, while the relative values of the μ_a and μ_c dipole moment components are in agreement with the intensities of the observed lines.

Internal Rotation of the HCF$_3$ Group

All of the measured transitions were split into two A,E component lines due to the hindered internal rotation of the HCF$_3$ group. Figure 1 shows the splitting details for the $3_{1,3}$-$2_{1,2}$ transition of the $C_2H_4O \cdots H^{13}CF_3$ isotopic species, measured

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Table 4. Internal Rotation Parameters of the Trifluoromethyl Group in Three Isotopomers of $C_2H_4O \cdots HCF_3$

	$C_2H_4O \cdots HCF_3$	$^{13}CCH_4O \cdots HCF_3$	$C_2H_4O \cdots H^{13}CF_3$
I_α/u Å^2	85.73(25)[a]	85.40(27)	84.58(44)
$\angle(a, i)^b$/deg	49.31(10)	50.18(18)	49.31(29)
$\angle(b, i)^b$/deg	[90.0][c]	[89.6][c]	[90.0][c]
$\angle(c, i)^b$/deg	40.69(10)	39.82(18)	40.69(29)
Δ_{AE}^d/MHz	0.68(1)	0.65(2)	0.69(2)
V_3/kJ mol^{-1}	0.546(4)	0.541(8)	0.545(8)
σ^e/kHz	6.7	4.5	3.2

[a] Standard error in parentheses in units of the last digits. [b] $\angle(g, i)$: angle between the inertial axes $g = a, b, c$ and the internal rotation axis i. [c] Parameters in square brackets were kept fixed in the fit to values calculated from the r_0 structure of Table 2. [d] Vibrational spacing between the E and A sublevels of the ground state. [e] Standard deviation of the fit.

in natural abundance. The 62 measured internal rotation splittings are collected in Table 1 of the Supporting Information.

The A−E splittings have been used to determine the internal rotation parameters,[27] that is: (i) the I_α moment of inertia of the HCF$_3$ top; (ii) the angles that the rotation axis of the HCF$_3$ top forms with the principal axes of inertia of the complex; (iii) the Δ_{AE} vibrational spacing between the E and A sublevels of the ground state; and (iv) the V_3 barrier to internal rotation of the HCF$_3$ top. All of these parameters, together with the standard deviation of the fit, are collected in Table 4 for the three isotopomers. The values of the determined internal rotor moment of inertia (see Table 2) are slightly smaller than the corresponding moment for the isolated HCF$_3$ of 89.23(2) u Å^2.[22] This confirms that the motion responsible for the A−E splittings is essentially the rotation of the HCF$_3$ group around an axis close to its C_3 symmetry axis.

As depicted in Figure 3, a 60° internal rotation of the HCF$_3$ group converts the global minimum configuration I into the transition state configuration II. Hence, the C−H⋯F−C interactions can be thought to be the cause of the experimental V_3 barrier of 0.546(4) kJ/mol, which represents the energy difference between forms I and II, that is, the difference in energy between two C−H⋯F−C interactions and one bifurcated interaction C−H⋯F⋯H−C. This value is smaller than the predicted ab initio values, 0.72 kJ/mol at the MP2/6-311+G(d, p) level and 0.90 kJ/mol at the MP2/6-311++G(2df, 2p) level. The experimental and ab initio V_3 values are in reasonable agreement, taking into account the different approximations made both in the treatment of the experimental A−E splittings and in the computational methods. This agreement supports the hypothesis that structure I corresponds to the global minimum of $C_2H_4O \cdots HCF_3$.

The internal rotation structural parameters given in Table 4 can be also compared to those of Table 2, derived from the experimental rotational constants. The angle $\angle(a, i) = 49.3°$, which defines the orientation of the internal rotor axis with respect to the a principal inertial axis, is comparable to the r_0 angle $\angle(a, C-H) = 56°$, defining the orientation of the trifluoromethane C−H bond. However, the small discrepancy suggests that the internal rotation of HCF$_3$ occurs around an axis not exactly coincident with its C_3 symmetry axis. The ab initio geometries calculated for the global minimum I and the transition structure II agree with such a description of the HCF$_3$ internal rotation. Thus, the angle $\angle(a, C-H)$ is calculated to be 59.7° for the global minimum (I) and 43.8° for the transition

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structure (II). The oscillation of the angle $\angle(a, C-H)$ during a 60° internal rotation is also consistent with the observed value of I_α, smaller than the corresponding I_c moment of inertia of isolated HCF_3.

Dissociation Energy

Six low energy vibrational modes are originated by the formation of the dimer, because the three translational and the three rotational degrees of freedom of one subunit disappear. We already could separate one of these motions, the internal rotation of the HCF_3 group, from the remaining five, and we obtained considerable information on it. The stretching of the centers of mass of the two constituent molecules can also be, in a first approximation, separated from the other vibrational modes. The remaining modes can be thought of as two bends and two residual internal rotations of the two moieties with respect to each other. For asymmetric top complexes in which the stretching coordinate is near-parallel to the inertial a-axis (condition nearly fulfilled for $C_2H_4O\cdots HCF_3$, see Figure 4), 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 the equation:[28]

$$k_s = 16\pi^4(\mu_D R_{CM})^2[4B_D{}^4 + 4C_D{}^4 - (B_D - C_D)^2(B_D + C_D)^2]/(hD_J) \quad (1)$$

where the suffix D stands for "dimer". So μ_D, B_D, and C_D are the reduced mass and the B and C rotational constants of the dimer. R_{CM} and D_J are the distance between the centers of mass of the two monomers and the first-order centrifugal distortion constant, respectively. The value $k_s = 6.0$ N/m has been obtained. The dissociation energy (E_D) has been evaluated to be 6.7 kJ/mol by assuming a Lennard-Jones potential function, using the approximate equation:[29]

$$E_D = (1/72)k_s R_{CM}{}^2 \quad (2)$$

The ab initio dissociation energy, corrected for basis set superposition error (BSSE) using the counterpoise procedure and including fragment relaxation,[30] is given in Table 3. The predicted value is more than 2 times the value calculated from the experimental data. We believe that our − experimentally related − value, even if rough, is more reliable than the theoretical value.

Nature of the C−H⋯O and C−H⋯F−C Interactions

The nature of the C−H⋯O and C−H⋯F−C interactions in the $C_2H_4O\cdots HCF_3$ complex can be inferred from the structural and energetic criteria usually employed to identify and classify the hydrogen bonds within their different categories.[1] The $r_{O\cdots H}$ distance is comparable to those found for dimethyl ether dimer ($r_{O\cdots H} = 2.53, 2.65$ Å)[17] and almost equal to that found for the complex $C_2H_4O\cdots HCCH$ ($r_{O\cdots H} \approx 2.4$ Å).[31] In the same way, the $r_{F\cdots H}$ distance is very close to the values found in the difluoromethane dimer ($r_{F\cdots H} = 2.64, 2.77$ Å).[16] These data show

that the $r_{O\cdots H}$ and $r_{F\cdots H}$ distances in $C_2H_4O\cdots HCF_3$ are within the range typical for WHB lengths.[1]

It is claimed that one of the main structural characteristics of the hydrogen bond is its directionality.[1,32] On the proton donor side, the directionality manifests itself as a preference for linearity ($\theta = 180°$) of the A−H⋯B group. However, even for moderate hydrogen bonds, the linearity is lost when secondary interactions bend the A−H⋯B fragment. This occurs for $C_2H_4O\cdots HCl$[33] ($\theta = 163.5°$) or oxetane⋯HCl[34] ($\theta = 168°$) where C−H⋯Cl secondary interactions take place. This nonlinearity is more pronounced as the hydrogen bond is weakened, as it happens for the series $C_2H_4O\cdots HCN$[35] ($\theta = 176°$) and $C_2H_4O\cdots HCCH$[31] ($\theta = 150°$), with the same kind of weak C−H⋯π secondary interactions. The marked nonlinearity of the C−H⋯O bond ($\theta = 118.4°$) in $C_2H_4O\cdots HCF_3$ is an indication of the importance of the C−H⋯F−C interactions. The nonlinearity of the C−H⋯O bond is indeed comparable to that of the C−H⋯F−C bonds ($\angle C-H\cdots F = 121.7°$), suggesting that all three bonds have the same nature and have binding energies that are similar in magnitude.

Hydrogen bonds are also directional at the proton acceptor side.[32] From this point of view, the directionality of hydrogen bonds can be identified with the orientation of electron lone pair domains. The observation of axial and equatorial hydrogen bond complexes in tetrahydropyran⋯HX,[25,36] pentamethylene sulfide⋯HX,[37] and thietane⋯HX[38] (X = F, Cl) in which HX points to the nonequivalent lone pair domains of the acceptor atoms (Y = O, S) is conclusive experimental evidence of the proton acceptor side directionality of the hydrogen bond. The C−H⋯O interaction in $C_2H_4O\cdots HCF_3$ corresponds to that picture. The trifluoromethane C−H bond is located in the plane bisector to the COC angle, points to one of the two equivalent lone pair domains of the oxygen atom, and keeps essentially this orientation during the internal rotation of the HCF_3 moiety in the complex. The angle $\varphi = 126°$, defining the proton acceptor directionality of C−H⋯O, is nearly equal to that observed for $C_2H_4O\cdots HCN$ ($\varphi = 128°$)[35] but is larger than the angles determined for complexes of C_2H_4O with strong proton donors as HCl ($\varphi = 103.2°$) or HF ($\varphi = 108.2°$).[33] This is consistent with the idea that proton acceptor directionality is softer for weak hydrogen bonds.[32] The corresponding angle defining the proton acceptor directionality for the C−H⋯F−C hydrogen bond is $\angle C-H\cdots F = 108°$, also close to a tetrahedral arrangement at the F atom.

The dissociation energy of $C_2H_4O\cdots HCF_3$ has been evaluated to be 6.7 kJ/mol. If the three C−H⋯O or C−H⋯F−C linkages which stabilize the adduct were equal, such a dissociation energy would correspond to a binding energy of about 2.2 kJ/mol for each of the weak bonds. This value coincides with that estimated for each of the three C−H⋯F−C bonds (2.2 kJ/mol) in the

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Table 5. Comparison of Force Constants of the Stretching Vibration of One Subunit with Respect to the Other, and of Binding Energies of $C_2H_4O\cdots HCF_3$ with Those of the Adducts Stabilized by WHB So Far Investigated by Rotationally Resolved Spectroscopy

	k_s/N m^{-1}	E_d/kJ mol^{-1}
$H_2C=O$ dimer[a]	6.2	4.8
difluoromethane dimer[b]	6.3	6.6
dimethyl ether dimer[c]	4.7	5.7
$C_2H_4O\cdots CF_3H$[d]	6.0	6.7

[a] Reference 39. [b] Reference 16. [c] Reference 17. [d] This work.

Table 6. Ab Initio Evidence for C−H Shortening and Blue Shifting upon WHB Formation in $C_2H_4O\cdots HCF_3$

Shortening of C−H Bond Lengths (Δl, Å)

	C_2H_4O or HCF_3	$C_2H_4O\cdots HCF_3$	Δl
$C-H_{HCF_3}$	1.0859	1.0839	−0.0031
$C-H_{C2H4O}$ (HB)	1.0861	1.0856	−0.0005[a]
$C-H_{C2H4O}$ (free)	1.0861	1.0857	−0.0004[a]

Blue Shift of C−H Stretchings ($\Delta\nu$, cm^{-1})

	C_2H_4O or CF_3H	$C_2H_4O\cdots CF_3H$	$\Delta\nu$
ν_{HCF3}	3223 (A$_1$)	3273 (A′)	+50[b]
ν_{C2H4O}	3263 (B$_1$)	3272 (A′)	+9[a]
	3249 (A$_2$)	3259 (A″)	+10[a]
	3158 (A$_1$)	3165 (A′)	+7[a]
	3151 (B$_2$)	3158 (A″)	+7[a]

[a] The four normal modes of the C−H vibrations in C_2H_4O have strong contributions from all four local C−H motions. As a consequence, all of them undergo the effects of the WHB formation. [b] $\Delta\nu$ is determined experimentally to be 24 cm^{-1} in ref 9.

difluoromethane dimer,[16] and it is very similar to that of the C−H$\cdots$O bonds (1.9 kJ/mol) in the dimethyl ether dimer.[17] We believe, however, that in the case of $C_2H_4O\cdots HCF_3$ the interaction energy of the C−H$\cdots$O H-bond is larger than that of the C−H$\cdots$F−C linkages. This consideration is suggested by the fact that $r_{O\cdots H}$ ($C_2H_4O\cdots CF_3H$) = 2.42 Å is shorter than $r_{O\cdots H}$ (dimethyl ether dimer) = 2.53, 2.65 Å,[17] while $r_{F\cdots H}$ ($C_2H_4O\cdots CF_3H$) = 2.74 Å is equal or larger than $r_{F\cdots H}$ (difluoromethane dimer) = 2.63, 2.76 Å.[16]

Table 5 compares the force constants and binding energies of the few molecular complexes, stabilized by WHB interactions, studied by rotationally resolved spectroscopy.[16,17,39] Each WHB does have, rather surprisingly, almost the same value, around 2 kJ/mol. All of these parameters have been obtained from the centrifugal distortion constant D_J.

Both structural and energy criteria indicate that the weak interactions H−C$\cdots$O and C−H$\cdots$F−C in $C_2H_4O\cdots HCF_3$ dimer are similar in nature to conventional hydrogen bonds and should be classified as a WHB. According to some recent findings, mainly by Hobza and collaborators,[8] these WHBs show peculiar properties such as a shortening of the C−H bond lengths and a blue shift of the stretching frequencies of the C−H groups involved in the H-bond. To verify these properties for C_2H_4-O$\cdots HCF_3$, we calculated its geometry and the vibrational frequencies, as well as those of isolated C_2H_4O and HCF_3 at the MP2/6-311+G(d,p) level by means of analytic Hessian matrix calculations. By comparing the geometries and the frequencies of the C−H groups involved in the H−Bond, before and after the formation of the adduct, we can observe a blue shift of the corresponding stretching vibrations, and a shortening of the C−H bond lengths, as shown in Table 6. The blue shift of the C−H bond in HCF_3 has been observed experimentally.[9] This allows us to classify the H−C$\cdots$O and C−H$\cdots$F−C interactions as improper, blue shifting H-bonds, in agreement with the definitions of Hobza and collaborators.[8]

Conclusions

This is, to our knowledge, the first report at a rotational resolution level on an adduct stabilized by three weak hydrogen bonds formed by two different subunits. Detailed information on the conformation, geometry, energetics, and properties of the WHBs has been obtained from the jet-cooled rotational spectrum, combined with ab initio calculations. The most interesting results of our investigation are as follows:

(1) Here, we show, thanks to the details underlying rotationally resolved spectroscopy and with the help of theoretical calculations, that both C−H$\cdots$O and C−H$\cdots$F−C interactions must be classified as WHBs. Previous investigations[9,12,18] on $C_2H_4O-CF_3H$ took into account only the C−H$\cdots$O, but not the C−H$\cdots$F−C WHB.

(2) We also show that the C−H$\cdots$F−C interactions are the cause of the V_3 barrier to internal rotation of the HCF_3 moiety in the complex, which we measured with very high precision.

(3) It seems that the cooperative effect of some WHBs is required to stabilize the adducts: in all three difluoromethane dimer, dimethyl ether dimer, and $C_2H_4O-CF_3H$ adducts, three WHBs are observed. It appears, in addition, that each single WHB contributes to E_D (the bonding energy of the complex) by ca. 2 kJ/mol.

(4) Experimental data from rotationally resolved spectroscopy are typically used as benchmarks to test the reliability of the various theoretical approaches. The comparison of the results of relatively high level calculations, such as MP2/6-311G(d,p) and MP2/6-311++G(2df, 2p) with BSSE corrections, with the experimental data indicates that the ab initio methods are quite good for geometry evaluations, but less precise to estimate the energies involved in the formation and in the internal dynamics of the complex.

We hope, using this investigation as an example, to have convincingly outlined the role of rotationally resolved spectroscopy in obtaining important chemical information.

Supporting Information Available: Table of experimental transition frequencies of three isotopic species of oxirane−trifluoromethane (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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