Weak Hydrogen Bonds

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Probing the C–H···π Weak Hydrogen Bond in Anesthetic Binding: The Sevoflurane–Benzene Cluster**

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Abstract: *Cooperativity between weak hydrogen bonds can be revealed in molecular clusters isolated in the gas phase. Here we examine the structure, internal dynamics, and origin of the weak intermolecular forces between sevoflurane and a benzene molecule, using multi-isotopic broadband rotational spectra. This heterodimer is held together by a primary C–H···π hydrogen bond, assisted by multiple weak C–H···F interactions. The multiple nonbonding forces hinder the internal rotation of benzene around the isopropyl C–H bond in sevoflurane, producing detectable quantum tunneling effects in the rotational spectrum.*

Weak hydrogen bonds are characterized by very low interaction energies ($< 20\ kJ\ mol^{-1}$), making these forces especially sensitive to modulation and cooperativity. Model molecular clusters formed by haloalkanes and small organic molecules reveal how C–H···O,[1] C–H···S,[2] C–H···N,[3] or C–H···F–C[4] interactions tend to associate to maximize the number and strength of nonbonding forces, as illustrated by the nine simultaneous C–H···F contacts in the cage structure of the difluoromethane trimer.[5] Much less structural information is available on the weaker (dispersion-dominated) C–H···π interaction, despite its significance in organic, organometallic, and biological chemistry. Reviews by Nishio[6] and Desiraju and Steiner[7] based most of their conclusions on crystallographic and ab initio studies. Alternatively, rotational spectroscopy recently analyzed several clusters involving phenyl π acceptors,[8–11] in absence of perturbing crystal or matrix effects. In particular, F_3CH···benzene[8] represents a prototypical C–H···π(Ph) interaction, with the C–H bond pointing to the center of the aromatic ring. However, the short hydrogen bonding distance $r_{(H\cdots Benzene)} = 2.366(2)$ Å suggests a stronger interaction than that with other π acceptors, prompting our interest in systems with a less acidic hydrogen atom, larger size, and the possibility of competing interactions.

The sevoflurane–benzene cluster is interesting from a chemical and biological point of view. Sevoflurane ($(CF_3)_2HC\text{-}O\text{-}CF_2H$) is a common volatile anesthetic and the sevoflurane–benzene cluster might model local interactions with aromatic side chains at the protein receptors.[12] Chemically, sevoflurane combines different donor and acceptor groups, including oxygen lone pairs, several C–F "organic fluorine" bonds (recognized as weak acceptors), and two kinds of activated isopropyl and fluoromethyl C–H bonds. Recently, van der Veken et al. studied the vibrational spectrum of sevoflurane–benzene, reporting the observation of two different species.[13] However, the interpretation of the experimental data was largely based in quantum chemical calculations. In comparison, our rotational study has identified 46 separate high-resolution spectra from distinct isotopologues, accurately resolving the molecular structure and the internal dynamics of the benzene ring.

The results of the conformational screening of sevoflurane–benzene can be found in Figure 1 and Table 1 (five lowest-energy conformers). The most stable conformations contain a variety of weak hydrogen-bonding effects, mostly based on C–H··· π interactions originating in the isopropyl and fluoromethyl groups, and in combinations of C–H···F and C–H···π weak contacts. The predicted global minimum (conformer 1) shows an intriguing topology for benzene not seen in other conformers, where the eclipsing of one hydrogen

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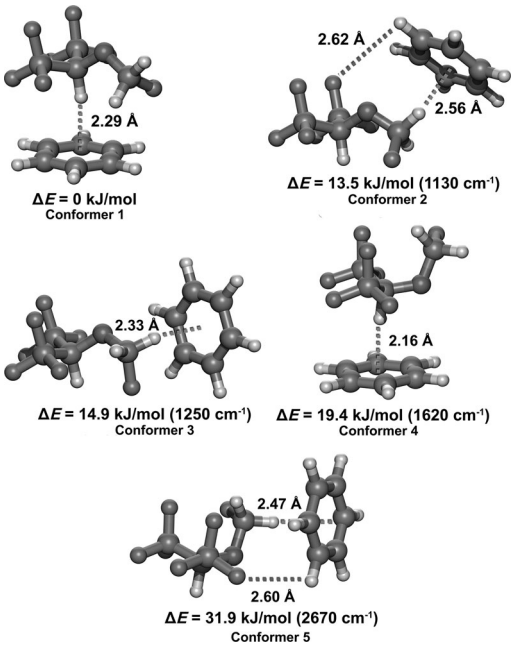

Figure 1. The predicted lowest-energy conformers of sevoflurane–benzene (MP2/6-311++g(d,p)).

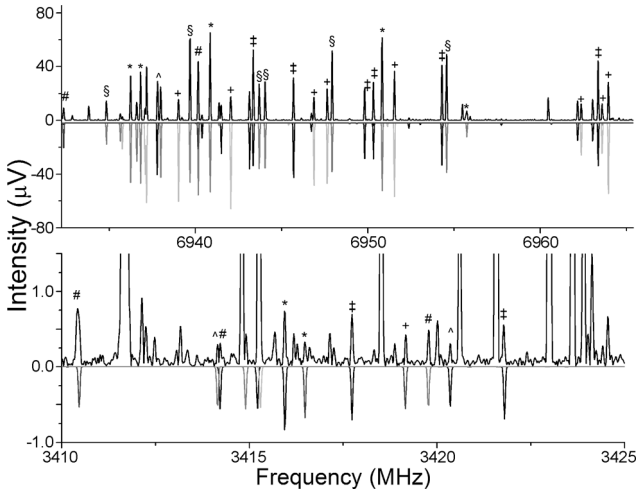

Figure 2. A section of the CP-FTMW spectrum of sevoflurane–[D_1]benzene (6.8 million acqusitions, positive traces). The six symbols correspond to a unique D isotopologue (negative traces for predictions). The bottom panel shows a selection of D/^{13}C double isotopologue transitions.

with the fluoromethyl group allows the other five hydrogens to be optimally staggered between the sevoflurane substituents. This arrangement makes it conceivable that some contribution arises from the two bifurcated and one single C–H···F interactions, which could enhance the attractive character of the primary C–H···π link. The simplicity of this optimally staggered C–H···π interaction is energetically favored by roughly 10.3–13.5 kJ mol^{-1}. Conformers 1 and 2 correspond to the observations of van der Veken et al., who found a population ratio of about 15:1 in favor of conformer 1 in Xe cryosolution, based on the intensities of the vibrational bands.[13]

The analysis of the rotational spectrum was possible thanks to recent advances in broadband (chirped-pulse) Fourier transform microwave (CP-FTMW) spectroscopy.[14,15] An overview of the 2–8 GHz MW spectrum is shown in Figure 2 and Figure S1 in the Supporting Information. The strongest transitions arise from the sevoflurane monomer (signal-to-noise ratio (SNR) ≈ 20000:1). The spectrum of the sevoflurane–benzene parent species was about 50 times weaker, more than sufficient to detect all independent spectra arising from each heavy-atom-monosubstituted isotopologue (^{13}C, ^{18}O) in natural abundance (0.2–1%). Hyperfine splittings were immediately noticeable in the transitions of the complex, and eventually attributed to the internal rotation of the benzene monomer about the sevoflurane frame. The

Table 1: Predictions for rotational parameters and energetics of the lowest-energy conformers of sevoflurane–benzene in Figure 1.[a]

	Theory (MP2/M06-2X/B3LYP—6-311++G(d,p))				
	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5
A [MHz]	508/515/500	650/670/636	663/698/636	543/557/538	685/697/667
B [MHz]	376/379/319	264/263/209	256/253/211	358/355/305	273/279/228
C [MHz]	353/358/302	235/235/191	234/233/193	325/318/281	229/234/196
$\lvert\mu_a\rvert$ [D]	2.2/2.3/2.1	1.9/2.3/2.1	1.1/1.3/2.1	1.1/1.0/1.1	1.6/1.8/1.6
$\lvert\mu_b\rvert$ [D]	0.5/0.3/0.2	0.6/0.4/0.8	1.3/1.7/0.8	0.8/0.8/0.9	1.1/1.0/1.1
$\lvert\mu_c\rvert$ [D]	1.6/1.6/1.7	1.3/1.3/1.2	1.3/1.0/1.2	1.3/1.3/1.3	0.5/0.6/0.6
$\lvert\mu_{TOT}\rvert$ [D]	2.7/2.8/2.7	2.4/2.6/2.6	2.2/2.3/2.6	1.8/1.8/1.9	2.0/2.1/2.1
D_J [kHz]	0.02/0.02/0.07	0.02/0.01/0.1	0.02/0.01/0.07	0.02/0.02/0.04	0.008/0.007/0.05
D_{JK} [kHz]	0.004/0.01/0.2	0.2/0.2/−0.3	0.1/0.2/−0.03	0.08/0.1/0.3	0.1/0.1/0.04
D_K [kHz]	0.04/0.04/0.3	0.1/0.1/0.4	0.8/0.2/0.1	−0.07/−0.1/−0.2	0.2/0.1/−0.02
d_1 [Hz]	−2.8/−2.8/−14.4	1.4/−1.6/−5.6	1.0/0.7/−3.4	−2.6/−3.3/−7.0	−0.8/−0.5/−7.0
d_2 [Hz]	0.2/0.2/−0.7	0.6/−0.1/−0.2	0.3/0.2/−0.2	−0.3/−0.2/−0.3	0.0/0.1/−0.5
ΔG [kJ mol^{-1}]	0.0/0.0/0.0	8.6/4.5/−1.5	7.9/10.2/0.1	19.0/13.8/17.0	31.0/22.7/17.8
$\Delta(E+ZPE)$ [kJ mol^{-1}]	0.0/0.0/0.0	13.5/10.3/2.2	14.9/13.5/2.2	19.4/17.0/15.5	31.9/24.6/18.5
E_d [kJ mol^{-1}]	−17.8/−31.1/−20.5	−12.8/−20.9/−5.0	−11.9/−19.1/−5.3	−17.4/−26.1/−5.6	−12.4/−20.6/−4.4

[a] Rotational constants (A, B, C), electric dipole moment components (μ_α, α = a, b, c), Watson's S-reduced centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2), Gibbs free energies at 298 K and 1 atm (ΔG), electronic energies with zero-point corrections ($\Delta(E+ZPE)$) and dissociation energies (E_d).

Table 2: Experimental rotational constants for the parent species and the benzene ^{13}C and D isotopologues of sevoflurane–benzene (full listing in the Supporting Information).

Species	*A* [MHz][a]	*B* [MHz]	*C* [MHz]	Δ_J [kHz][b]	Δ_{JK} [kHz]	Δ_K [kHz]	*N*[c]	RMS [kHz]
parent (*A*)	508.42070(40)[d]	358.82931(13)	338.32685(13)	[0.03490]	[0.0550]	[−0.0630]	77	6.04
parent (*B*)	507.74250(60)	358.82020(12)	338.30995(12)	"	"	"	107	6.41
parent (avg)	508.08160(50)	358.82476(13)	338.31840(13)	"	"	"	–	–
5-D	505.704895(85)	356.433250(86)	335.438320(92)	0.03490(44)	0.0550(14)	−0.0630(16)	225	6.91
1-D	505.425300(95)	355.461685(38)	335.793300(41)	"	"	"	175	6.24
2-D	504.157430(60)	357.392938(38)	335.338172(35)	"	"	"	254	7.13
3-D	503.901760(58)	356.776863(34)	336.551764(34)	"	"	"	247	6.37
4-D	504.480480(54)	355.830667(33)	337.133881(31)	"	"	"	272	6.57
6-D	506.345460(81)	355.463814(29)	335.477671(28)	"	"	"	188	4.81
5-^{13}C	506.7452(77)	356.63733(29)	336.95711(22)	[0.03490]	[0.0550]	[−0.0630]	49	6.15
1-^{13}C	507.7542(70)	356.32317(20)	336.13907(22)	"	"	"	57	5.23
2-^{13}C	507.2520(41)	356.44752(14)	336.24013(15)	"	"	"	52	3.53
3-^{13}C	506.5724(49)	357.20783(16)	336.21528(17)	"	"	"	52	3.74
4-^{13}C	506.3589(71)	357.04374(21)	336.76461(21)	"	"	"	59	5.96
6-^{13}C	507.3754(94)	356.67671(27)	336.29174(30)	"	"	"	56	6.09

[a] Rotational parameters as defined in Table 1. [b] Centrifugal distortion fixed to the values for the 5-D isotopologue. [c] Number of measured transitions (*N*) and RMS deviation of the fit (frequency accuracy 10 kHz). [d] Standard error in parentheses in units of the last digit.

symmetry point group of the internal rotor is C_6, which contains four irreducible representations (A, B, E_1, and E_2). Therefore, each rotational transition is split into four separate symmetry components. We collect in Table 2 the experimental rotational constants derived for the parent species, for which the sixfold internal rotation barrier was determined as $V_6 = 32.8687(27)$ cm^{-1}. The details of the barrier calculation will be reported separately. Isotopic substitutions in sevoflurane are similarly complicated by the internal rotation. However, substitutions on benzene break its C_6 symmetry, resulting in simpler asymmetric-top spectra. Our strategy was thus based on the use of a sample of monodeuterated benzene, allowing a manageable assignment of all the sevoflurane isotopologues in the cluster. The sensitivity of the experiment was so high that the doubly substituted D/^{13}C isotopologues in natural abundance could be detected with good intensity (e.g. SNR $\geq$ 3:1). Finally, and despite the extremely high spectral density, 33 of the 60 possible D/^{13}C isotopologues were assigned and every carbon had at least one associated isotopologue assignment. The spectral assignment was aided by automatic routines developed in Virginia.[16] The rotational parameters and experimental transitions for all 46 measured species are presented in Table 2 and Tables S1–S47 in the Supporting Information. No other conformations of sevoflurane–benzene were detected. Two sevoflurane homodimers will be reported separately.

The analysis of the multi-isotopic rotational spectra led to an accurate experimental structure for the cluster, including all heavy atoms and the six benzene hydrogens. Application of Kraitchman's equations[17] confirmed that the sevoflurane monomer[18] is not distorted upon complexation, as usually assumed for weak and moderately strong hydrogen bonds. Later, a least-squares fitting resulted in the ground-state-effective (r_0) structure.[19,20] The dimer has $3N-6 = 75$ independent degrees of freedom for a total of 138 experimental observations (three moments of inertia per species). Therefore, sevoflurane–benzene offers the possibility to determine a nearly full effective structure for a molecular complex, which is very rare. On assumption of ab initio constraints (M06-2X, Table S48) only for the positions of the three sevoflurane hydrogens and F-C-F bond angles, the molecular structure of Table S49 was obtained. A comparison with the theoretical geometries can be found in Figure 3, Figures S2 and S3, and Table S50. Interactive three-dimensional PDF representations can be found in Figures S4–S6.

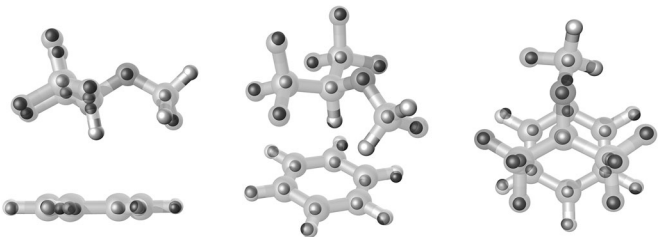

Figure 3. Views of the sevoflurane–benzene structure. The ball-and-stick frameworks correspond to the M06-2X/6-311++g(d,p) geometry. The small spheres represent the experimental r_0 structure.

Consequently, we have addressed the structure, internal dynamics, and origin of the weak unions between sevoflurane and a benzene molecule through multi-isotopic rotational spectra. A single conformation was observed in the cold ($T_{rot} \approx 2$ K) supersonic jet, corresponding to the predicted global minimum primarily bound through the isopropyl C–H bond of sevoflurane. There is no indication of the second species with fluoromethyl bonding suggested from a weak band in the low-resolution IR spectra,[13] either because of thermal depopulation, or because of conformational relaxation in the jet. The C–H···π(Ph) weak hydrogen bond $r_{(H\cdots Benzene)} = 2.401(16)$ Å is slightly longer than that in the complex with trifluoromethane ($r_{(H\cdots Benzene)} = 2.366(2)$ Å), but still reflects the important activation role of the electronegative F and O atoms. The electrostatic contribution due to the interaction of the acidic hydrogen and the Lewis basic π benzene cloud likely enhances the C–H···π interaction with respect to

aliphatic systems.[21] The geometry of the complex suggests that the main C–H···π interaction is modulated by secondary C–H···F weak contacts between three aromatic hydrogens and the fluorine atoms in sevoflurane. The calculated distances for the secondary interactions range from 3.095(14) Å in $OCH_2F\cdots H_1$ to 3.293(12)–3.531(15) Å in $CF_3\cdots H$ interactions. These values are 0.5–1 Å longer than the conventional fluorine hydrogen-bonding distances, but not unreasonable for bifurcated or secondary weak hydrogen bonds, as bonding distances up to 2.876–3.246 Å were identified in the difluoromethane trimer[5] and related clusters.[1-4] It is thus likely that the multiple weak fluorine hydrogen bonds are a contributor to the relative staggered orientation of the benzene ring and sevoflurane. An additional argument originates from the barrier hindering the internal rotation of the benzene moiety, which strikingly compares with the free torsion between the two subunits of $F_3CH\cdots$benzene.

The theoretical data outline the difficulty to treat dispersion forces. The B3LYP method fails to reproduce the cluster geometry, as first observed by a poor agreement with the rotational constants. The B3LYP C–H···π hydrogen bond is roughly 0.5 Å longer than the experimental value and it predicts the ring to be slightly tilted with respect to the C–H bond (98°). Conversely, the MP2 and M06-2X values (92.3° and 91.9°, respectively) agree fairly well with the r_0 determination (92.65(43)°). Significantly, in B3LYP the benzene ring is actually rotated approximately 25° from the eclipsing orientation of the global minimum. Thus, this optimal staggering is actually dependent on the proper treatment of the dispersion contribution to the C–H···π weak hydrogen bond. These results suggest that both electrostatics and dispersion play important roles in determining the complexation geometry of sevoflurane–benzene. Similar discrepancies of B3LYP were observed for $(phenol)_2$.[10] In comparison, the MP2 and M06-2X methods with a modest Pople triple-ζ basis set acceptably account for the spectral results. MP2 and M06-2X mostly differ by a slight rotation in the benzene orientation, which could be attributed to the low-lying benzene torsional mode (14 cm^{-1}).

In conclusion, the new developments in broadband rotational spectroscopy lead to unparalleled levels of sensitivity for molecules and molecular clusters of increasing size (> 10–20 heavy atoms). A theoretical methodology with a balance between accuracy, computational cost, and portability is crucial for further experiments. As a result, rotational studies are essential in benchmarking the theoretical procedures for efficient description of weak nonbonding forces.

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