Microwave spectroscopy and characterization of the helical conformer of perfluorohexane

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This paper is dedicated to William F. Bailey in honor of his 65th birthday

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Abstract
The lowest energy conformer of perfluorohexane (C₆F₁₄) is helical and its microwave rotational spectrum has been observed and assigned. The helicity along the carbon chain results in overall C₂ symmetry with the C₂ axis corresponding to the c-principal axis. The assignment of a c-type spectrum confirms the structure of C₆F₁₄ to be helical. The rotational constants are A 824.9001(9) MHz, B 202.2195(8) MHz, and C 198.3355(10) MHz. The molecular parameters were characterized by scaling computed models by the square root of the ratio of the observed second moments to those computed. The scaled structures exactly reproduce the observed second moments. From this scaling approach, the exterior C₁C₂C₃C₄ dihedral angle is 16.7° and the interior C₂C₃C₄C₅ dihedral angle is 18.0° away from trans. Computed models at the PBE0/VTZ level of theory are in excellent agreement with the experimental results.

Keywords: Perfluorohexane, tetradecafluorohexane, molecular structure, microwave spectroscopy

Introduction
The polymer polytetrafluoroethylene (PTFE) is well characterized and known to have a helical structure by X-ray diffraction studies on single fibers.¹ A helix can be described by either a helical perspective or a molecular perspective. In the helical perspective, the helix is defined by the following three parameters: the distance from each atom to the helical axis (the helical radius), ρ; the helical angle about the helical axis, θ; and the translation from one atom to the next (pitch) along the helical axis, d. In the molecular perspective, the helix is defined as follows: the C-C bond length, r; the CCC bond angle, φ; and the CCCC dihedral angle, τ. A visual
representation of the two perspectives is displayed in Figure 1. The mathematical relationships for converting between the two perspectives are given in Equations 1 and 2.\textsuperscript{2,3} For the low temperature (\(<19\,^{\circ}\text{C}\)) phase II form of PTFE, the helical angle is periodic and equal to 13.8\(^{\circ}\).\textsuperscript{4} This corresponds to a CCCC dihedral angle of about 17\(^{\circ}\) away from trans. The helicity of PTFE is attributed to steric and dipole repulsions of F atoms on alternate carbons. A small helical twist along the carbon chain helps alleviate these repulsions (Figure 2).

\textbf{Figure 1.} Helical (left) and molecular (right) perspectives for describing a helix. The dashed line represents the helical axis and the green circles represent CF\(_2\) groups.

\textbf{Figure 2.} Top view of C\(_6\)F\(_{14}\).

Experimental and computational studies on smaller perfluoroalkane oligomers also show the lowest energy structures to be helical, beginning with perfluorobutane (C\(_4\)F\(_{10}\)).\textsuperscript{5-15} The helical (trans), gauche, and ortho (\(\tau \sim 90^{\circ}\)) conformers of C\(_4\)F\(_{10}\) were observed by nitrogen matrix-isolated IR spectroscopy.\textsuperscript{6} Only the gauche form was observed in a microwave study,\textsuperscript{16} with the
helical form apparently having too small a dipole moment to be observable and the ortho form relaxing to the lower energy gauche form.\textsuperscript{17} The CCCC dihedral angle of \( \text{C}_4\text{F}_{10} \) has not been determined experimentally and computations predict a twist of \( \sim 14^\circ \) from trans.\textsuperscript{6-13}

\[
\cos \theta = \frac{1}{2}(-\cos \phi + \cos \tau - \cos \phi \cos \tau - 1)
\]
\[
d^2 = r^2(1 - \cos \tau)(1 - \cos \phi)/(3 + \cos \phi - \cos \tau + \cos \phi \cos \tau)
\]
\[
\rho^2 = 2r^2(1 + \cos \phi)/(3 + \cos \phi - \cos \tau + \cos \phi \cos \tau)^2
\]

(1)

\[
r^2 = d^2 + 4\rho^2 \sin^2(\theta/2)
\]
\[
\cos(\phi/2) = (1 - d^2/r^2)^{1/2} \sin(\theta/2)
\]
\[
\tan(\tau/2) = (d/r) \tan(\theta/2)
\]

(2)

The microwave spectra of perfluoropentane (\( \text{C}_5\text{F}_{12} \)) and its three \( ^{13}\text{C} \) isotopomers have recently been assigned.\textsuperscript{15} The value of the dihedral angle was determined by scaling computed models to exactly reproduce the observed second moments. The CCCC dihedral angle was calculated to be \( 17^\circ \pm 1^\circ \) from trans using this method, in good agreement with previous computational studies.\textsuperscript{7,9-14} In the same study, the structure of perfluoropropane (\( \text{C}_3\text{F}_8 \)) was found to be non-helical (\( C_{2v} \)). Apparently, the steric and dipole interactions in the three carbon chain are not sufficient to cause a twist in the structure.

To continue characterization of short perfluoroalkanes, a microwave spectroscopic study on perfluorohexane (\( \text{C}_6\text{F}_{14} \)) was performed. The two CCCC dihedral angles in \( \text{C}_6\text{F}_{14} \) are predicted to be about \( 16^\circ-18^\circ \) away from trans by various computational methods.\textsuperscript{7,11,12,14} \( \text{C}_6\text{F}_{14} \), if helical, would have a dipole moment and, therefore, be observable by microwave spectroscopy. The microwave spectrum of the lowest energy helical conformer of \( \text{C}_6\text{F}_{14} \) (Figures 2 and 3) has been observed and assigned and the molecular geometry analyzed.

![Figure 3](image)

**Figure 3.** The \( C_{2h} \) structure of \( \text{C}_6\text{H}_{14} \) with dihedral angles of \( 180^\circ \) (left) and the \( C_2 \) structure of \( \text{C}_6\text{F}_{14} \) with dihedral angles of \( \sim 17^\circ \) from trans (right).
Results and Discussion

The lowest energy all trans conformer of n-hexane ($C_{2h}$) lacks a dipole moment and is therefore spectroscopically unobservable. The lowest energy all trans structure of perfluoroalkanes, beginning with $C_4F_{10}$, is helical. A figure of the helical structure of $C_6F_{14}$, similar to Figure 3, given in reference 14 sparked our interest as this structure clearly has a dipole moment. The helicity of perfluoroalkanes results in structures with overall $C_2$ symmetry. For an odd numbered chain, like $C_5F_{12}$, the $C_2$ axis corresponds to the b-axis and b-type transitions are observed. For an even numbered chain the $C_2$ axis becomes the c-axis and, thus, c-type transitions are expected for $C_6F_{14}$. The observation and assignment of the microwave spectrum of $C_6F_{14}$ to c-type transitions (see Table 1 and Supplementary Table 1) unambiguously shows that the lowest energy structure of $C_6F_{14}$ is helical. The observation of c-type transitions requires that the molecule have a non-zero dipole moment along the c axis. If the molecule were non-helical, the structure would have $C_{2h}$ symmetry and no dipole moment along any principal axis.

Table 1. Spectroscopic constants of $C_6F_{14}$

<table>
<thead>
<tr>
<th></th>
<th>$C_6F_{14}$</th>
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<tbody>
<tr>
<td>A/MHz</td>
<td>824.9001(9)</td>
</tr>
<tr>
<td>B/MHz</td>
<td>202.2195(8)</td>
</tr>
<tr>
<td>C/MHz</td>
<td>198.3355(10)</td>
</tr>
<tr>
<td>$D_J$/kHz</td>
<td>0.00165(13)</td>
</tr>
<tr>
<td>$P_{ab}$/uÅ²</td>
<td>2217.304</td>
</tr>
<tr>
<td>$P_{bb}$/uÅ²</td>
<td>330.798</td>
</tr>
<tr>
<td>$P_{cc}$/uÅ²</td>
<td>281.857</td>
</tr>
<tr>
<td>Kappa</td>
<td>-0.9876022</td>
</tr>
<tr>
<td>No. Lines</td>
<td>46</td>
</tr>
<tr>
<td>Std. Dev./kHz</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The structure of $C_3F_8$ was recently determined to be non-helical ($C_{2v}$). The $P_{cc}$ second moment is 134.338 u Å², or 44.78 u Å² per CF$_2$/CF$_3$ group. Assuming transferability, $C_6F_{14}$ would have a $P_{cc}$ of 6 x 44.78 or 268.68 u Å² if it exhibited $C_{2h}$ symmetry. The observed $P_{cc}$ is 281.857 u Å², or 46.98 u Å² per CF$_2$/CF$_3$ group. This increase in $P_{cc}$ also confirms the helical structure of $C_6F_{14}$ because C atoms as well as F atoms lie outside the ab plane and contribute to $P_{cc}$. The $P_{cc}$ second moment increases steadily as the C chain becomes longer. The $P_{cc}$ per CF$_2$/CF$_3$ group for $C_3F_8$ is 44.78 u Å² and is predicted to be 45.16 u Å² for $C_4F_{10}$ (from PBE0/VTZ calculations). This value increases to 45.92 u Å² for $C_5F_{12}$ and to 46.98 u Å² for $C_6F_{14}$. The trend demonstrates that as the C chain length increases more mass is displaced outside the ab plane and contributes to $P_{cc}$ due to the helicity of the structures.

The microwave data alone do not allow for an exact determination of the CCCC dihedral angles. To analyze the structural parameters of $C_6F_{14}$, the principal coordinates of the computed
model were scaled by the square root of the ratio of the observed second moments to the computed second moments. This shifts the coordinates of each atom to exactly reproduce the observed second moments. Computations were performed at the PBE0/VTZ level of theory using the Gaussian 03 program. The PBE0 functional has been shown to accurately model perfluoroalkanes and is again evident by the excellent agreement between the observed and computed spectroscopic constants for C₆F₁₄ (Table 2). The scale factors are 0.99996 for the a-coordinates, 1.00167 for the b-coordinates, and 1.00288 for the c-coordinates. Since the scale factors are nearly equal to 1, the structural parameters do not change much from the computed model (Table 3). The overall C₂ symmetry of C₆F₁₄ allows for two distinct dihedral angles. The exterior C₁C₂C₃C₄ dihedral angle (also equal to C₃C₄C₅C₆) is 16.7° away from trans and the interior C₂C₃C₄C₅ dihedral angle is 18.0° away from trans using this scaling approach. The exterior dihedral angle is in agreement with the single dihedral angle of about 17° from trans determined in C₅F₁₂ using this same scaling approach. The interior dihedral angle is slightly larger than the exterior dihedral angle likely because the interior of the molecule is more sterically crowded.

**Table 2.** Comparison of observed spectroscopic constants to the computed and scaled models

<table>
<thead>
<tr>
<th></th>
<th>Obs'd</th>
<th>PBE0/VTZ</th>
<th>Scaled PBE0/VTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/MHz</td>
<td>824.9001</td>
<td>828.6</td>
<td>824.90</td>
</tr>
<tr>
<td>B/MHz</td>
<td>202.2195</td>
<td>202.3</td>
<td>202.22</td>
</tr>
<tr>
<td>C/MHz</td>
<td>198.3355</td>
<td>198.4</td>
<td>198.34</td>
</tr>
<tr>
<td>Pₐₙ¹/uÅ²</td>
<td>2217.304</td>
<td>2217.5</td>
<td>2217.30</td>
</tr>
<tr>
<td>Pₐₜ¹/uÅ²</td>
<td>330.798</td>
<td>329.7</td>
<td>330.80</td>
</tr>
<tr>
<td>Pₜₜ¹/uÅ²</td>
<td>281.857</td>
<td>280.2</td>
<td>281.86</td>
</tr>
</tbody>
</table>

**Table 3.** Selected structural parameters from the computed and scaled models

<table>
<thead>
<tr>
<th></th>
<th>PBE0/VTZ</th>
<th>Scaled PBE0/VTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁-C₂</td>
<td>1.555</td>
<td>1.556</td>
</tr>
<tr>
<td>C₂-C₃</td>
<td>1.558</td>
<td>1.559</td>
</tr>
<tr>
<td>C₃-C₄</td>
<td>1.561</td>
<td>1.561</td>
</tr>
<tr>
<td>C₄C₅</td>
<td>114.0</td>
<td>113.9</td>
</tr>
<tr>
<td>C₃C₄C₅</td>
<td>113.0</td>
<td>112.9</td>
</tr>
<tr>
<td>C₁C₂C₃C₄</td>
<td>16.7</td>
<td>16.7</td>
</tr>
<tr>
<td>C₂C₃C₄C₅</td>
<td>18.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>

The scaled C₆F₁₄ structure was converted to helical parameters using Equations 1 and 2 above, averaging bond lengths, bond angles, and the dihedral angles. The helical radius ρ is 0.434 Å, the helical angle θ is 14.3°, and the pitch d is 1.298 Å. These values are in reasonable
agreement with the 0.42 Å helical radius, 13.8° helical angle, and 1.292 Å pitch of the low temperature phase II form of PTFE. By comparison, the determined helical parameters of C₅F₁₂ from a scaled MP2/VTZ model are 0.431 Å helical radius, 14.1° helical angle, and 1.297 Å pitch.

Conclusions

The helical structure of C₆F₁₄ has been observed by assignment of its c-type rotational spectrum, consistent with overall C₂ symmetry. The structure was characterized by scaling a PBE0/VTZ computed model to exactly reproduce the observed second moments. The scaled structure has a C₁C₂C₃C₄ exterior dihedral angle of 16.7° from trans and a C₂C₃C₄C₅ interior dihedral angle of 18.0° from trans. In terms of helical parameters C₆F₁₄ has a helical angle of about 14°, in good agreement with the 13.8° helical angle of the low temperature phase II form of PTFE.

Experimental Section

General. C₆F₁₄ was purchased from Synquest Laboratories and studied directly. Vapor of the sample was transferred to a 7 L stainless steel tank to a pressure of 0.04 atm. 6.5 atm He was added to produce a 0.6% sample mixture. Pulses of the sample mixture at 1.75 atm were admitted at 5 Hz into the pulsed-jet Fourier transform microwave spectrometer of the Southern New England Microwave Consortium. Five microwave pulses were observed per gas pulse and rotational transitions were measured in the 6-11 GHz range, although the complete spectrum was not scanned. Transitions were observed as Doppler doublets with estimated uncertainties to be about 2 kHz. The rotational temperature of the expanded gas is estimated to be about 5 K. Three observed transitions at 7624.38 MHz, 8024.94 MHz, and 8425.50 MHz were tentatively assigned to the 5₅₀-4₄₀/5₅₁-4₄₁, 6₅₁-5₄₁/6₅₂-5₄₂, and 7₅₂-6₄₂/7₅₃-6₄₃ degenerate pairs, respectively. This tentative assignment predicted the 8₅₃-7₄₃/8₅₄-7₄₄ degenerate transitions to be around 8826 MHz. The assignment proved to be correct as a line was observed at 8826.05 MHz, and several more of these degenerate pairs were measured. Since the transitions are doubly degenerate, B and C are not distinguishable. A host of non-degenerate lines were predicted from the new assignment and were measured to distinguish B and C. The transitions were fit using rotational constants and one quartic centrifugal distortion constant using Watson’s S reduction to an rmsd of 1.8 kHz. The use of only one centrifugal distortion constant that is quite small indicates that C₆F₁₄ is very rigid. The observed spectroscopic constants are displayed in Table 1 and the 46 assigned transitions are listed in Supplementary Table 1.
Acknowledgments

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References