

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

DOI: <http://dx.doi.org/10.3998/ark.5550190.0012.502>

Abstract

The lowest energy conformer of perfluorohexane (C_6F_{14}) is helical and its microwave rotational spectrum has been observed and assigned. The helicity along the carbon chain results in overall C_2 symmetry with the C_2 axis corresponding to the c-principal axis. The assignment of a c-type spectrum confirms the structure of C_6F_{14} 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 $C_1C_2C_3C_4$ dihedral angle is 16.7° and the interior $C_2C_3C_4C_5$ 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.^{2,3} For the low temperature (<19 °C) phase II form of PTFE, the helical angle is periodic and equal to 13.8°.⁴ This corresponds to a CCCC dihedral angle of about 17° 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).

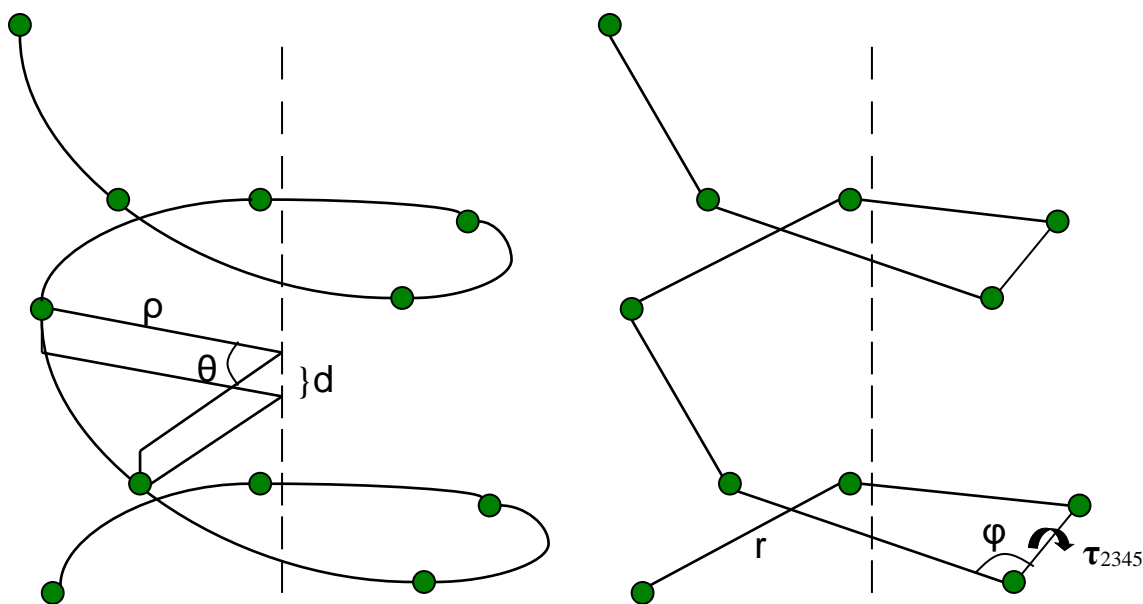


Figure 1. Helical (left) and molecular (right) perspectives for describing a helix. The dashed line represents the helical axis and the green circles represent CF_2 groups.

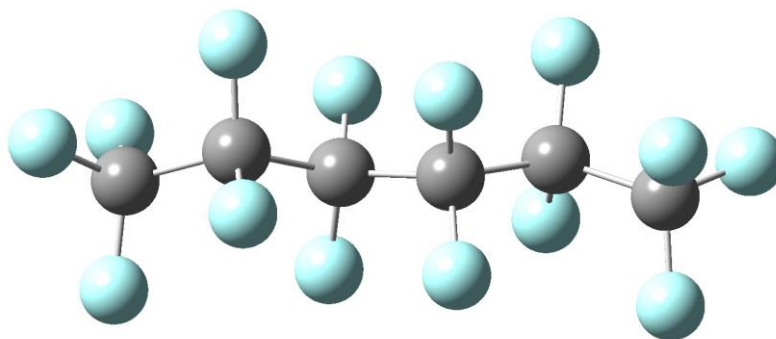


Figure 2. Top view of C_6F_{14} .

Experimental and computational studies on smaller perfluoroalkane oligomers also show the lowest energy structures to be helical, beginning with perfluorobutane (C_4F_{10}).⁵⁻¹⁵ The helical (trans), gauche, and ortho ($\tau \sim 90^\circ$) conformers of C_4F_{10} were observed by nitrogen matrix-isolated IR spectroscopy.⁸ Only the gauche form was observed in a microwave study,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.¹⁷ The CCCC dihedral angle of C₄F₁₀ has not been determined experimentally and computations predict a twist of ~14° from trans.⁶⁻¹³

$$\begin{aligned}\cos\theta &= \frac{1}{2}(-\cos\varphi + \cos\tau - \cos\varphi \cos\tau - 1) \\ d^2 &= r^2(1 - \cos\tau)(1 - \cos\varphi)/(3 + \cos\varphi - \cos\tau + \cos\varphi \cos\tau) \\ \rho^2 &= 2r^2(1 + \cos\varphi)/(3 + \cos\varphi - \cos\tau + \cos\varphi \cos\tau)^2\end{aligned}\quad (1)$$

$$\begin{aligned}r^2 &= d^2 + 4\rho^2\sin^2(\theta/2) \\ \cos(\varphi/2) &= (1 - d^2/r^2)^{1/2}\sin(\theta/2) \\ \tan(\tau/2) &= (d/r) \tan(\theta/2)\end{aligned}\quad (2)$$

The microwave spectra of perfluoropentane (C₅F₁₂) and its three ¹³C isotopomers have recently been assigned.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° ± 1° from trans using this method, in good agreement with previous computational studies.^{7,9-14} In the same study, the structure of perfluoropropane (C₃F₈) 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 (C₆F₁₄) was performed. The two CCCC dihedral angles in C₆F₁₄ are predicted to be about 16°-18° away from trans by various computational methods.^{7,11,12,14} C₆F₁₄, if helical, would have a dipole moment and, therefore, be observable by microwave spectroscopy. The microwave spectrum of the lowest energy helical conformer of C₆F₁₄ (Figures 2 and 3) has been observed and assigned and the molecular geometry analyzed.

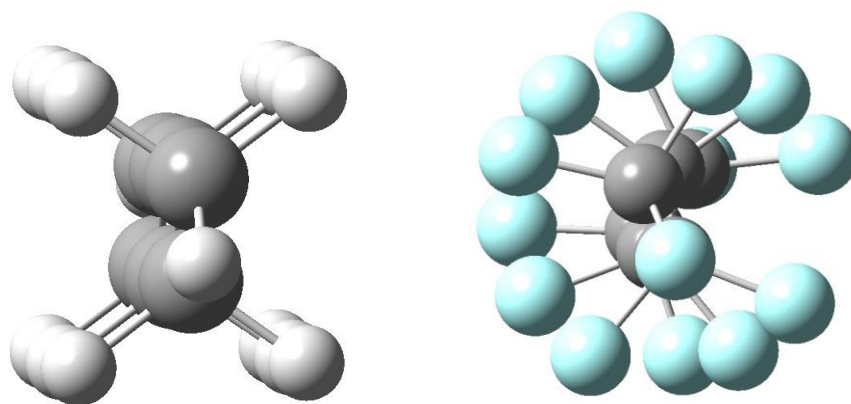


Figure 3. The C_{2h} structure of C₆H₁₄ with dihedral angles of 180° (left) and the C₂ structure of C₆F₁₄ with dihedral angles of ~17° from trans (right).

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} ,¹⁵ 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}

	C_6F_{14}
A/MHz	824.9001(9)
B/MHz	202.2195(8)
C/MHz	198.3355(10)
D _J /kHz	0.00165(13)
P _{aa} /uÅ ²	2217.304
P _{bb} /uÅ ²	330.798
P _{cc} /uÅ ²	281.857
Kappa	-0.9876022
No. Lines	46
Std. Dev./kHz	1.8

The structure of C_3F_8 was recently determined to be non-helical (C_{2v}).¹⁵ The P_{cc} second moment is 134.338 u Å², or 44.78 u Å² per CF₂/CF₃ 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 CF₂/CF₃ 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 CF₂/CF₃ group for C_3F_8 ¹⁵ 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} ¹⁵ 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.¹⁸ The PBE0 functional has been shown to accurately model perfluoroalkanes^{13,15} 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.¹⁵ 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

	Obs'd	PBE0/VTZ	Scaled PBE0/VTZ
A/MHz	824.9001	828.6	824.90
B/MHz	202.2195	202.3	202.22
C/MHz	198.3355	198.4	198.34
P _{aa} /uÅ ²	2217.304	2217.5	2217.30
P _{bb} /uÅ ²	330.798	329.7	330.80
P _{cc} /uÅ ²	281.857	280.2	281.86

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

	PBE0/VTZ	Scaled PBE0/VTZ
C ₁ -C ₂	1.555	1.556
C ₂ -C ₃	1.558	1.559
C ₃ -C ₄	1.561	1.561
∠C ₁ C ₂ C ₃	114.0	113.9
∠C ₃ C ₄ C ₅	113.0	112.9
C ₁ C ₂ C ₃ C ₄	16.7	16.7
C ₂ C ₃ C ₄ C ₅	18.0	18.0

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.³ 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.¹⁵

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 spectrometer¹⁹ of the Southern New England Microwave Consortium.²⁰ 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 reduction²¹ 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

Dan Frohman, Andrea Minei, and Stewart Novick of Wesleyan University provided generous assistance with the microwave spectrometer. John Montgomery, Jr. provided assistance with the computations and scaling. NSF provided funds for construction of the spectrometer.

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