

Structure and Dipole Moment of $(\text{CF}_3)_3\text{CC}\equiv\text{CH}$

K. K. LEHMANN,* F. J. LOVAS,† AND R. D. SUENRAM†

* *Department of Chemistry, Princeton University, Princeton, New Jersey 08544; and †Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

The microwave spectrum of $(\text{CF}_3)_3\text{CCCH}$ has been recorded on the NIST Fourier-transform microwave spectrometer. The rotational constant for the principal isotopomer is found to be $B_0 = 690.87916(4)$ MHz and the dipole moment $\mu_0 = 2.038(8)$ Debye. The microwave spectra of the three species with ^{13}C substitution on the symmetry axis were observed in natural abundance. Combining rotational constants with the CF bond length and FCF bond angles previously determined in $(\text{CF}_3)_3\text{CH}$ and $(\text{CF}_3)_3\text{CI}$ by electron diffraction, the bond lengths and bond angle around the central carbon atom could be determined and are in good agreement with the above mentioned molecules. © 1993 Academic Press, Inc.

As part of an ongoing study of intramolecular vibrational relaxation in terminal acetylene compounds (1), a study of the compound $(\text{CF}_3)_3\text{CC}\equiv\text{CH}$ (perfluoro-*t*-butylacetylene) was initiated. The microwave spectrum of this symmetric top molecule has not been previously reported, and an analysis of the rotational spectrum of the ground vibrational state will enable future microwave-infrared double resonance experiments to be carried out. The spectral analysis was performed using a pulsed nozzle in a Balle–Flygare-type Fourier-transform microwave spectrometer (2) which has been described previously (3). The microwave spectrum has yielded information on the structure as well as the dipole moment of the molecule.

The sample was prepared in a custom synthesis by Solidarity Associates¹ and was used as provided. Both ^1H and ^{19}F NMR showed only one peak, and the IR spectrum was consistent with the expected compound. The sample was diluted to about 0.3% in Ar and expanded through the pulsed molecular beam valve at a backing pressure of about 235 kPa (20 psi).

The rotational transitions of the principal isotope were observed as listed in Table I. The transitions span the rotational quantum numbers ranging from $J = 7 \leftarrow 6$ through $J = 13 \leftarrow 12$. The K structure was unresolved on all of the transitions. The transitions were fit to the expression $\nu(J + 1 \leftarrow J) = 2B(J + 1) - 4D(J + 1)^3$ with a standard deviation of 2.1 kHz. The resulting constants are listed in Table II. The electric dipole moment was measured by using both first- and second-order Stark effects. The first-order Stark effect of the $KM = 1, 2,$ and 3 transitions for the $J = 7 \leftarrow 6$ rotational transition were observed at electric fields of 30.93 and 32.48 V/cm. For a description of the experimental techniques involved in the Stark analysis using a Balle–Flygare-type spectrometer, see Ref. (4). A fit, with $\sigma = 1$ kHz, yields an electric dipole moment of $6.798(27) \times 10^{-30} \text{ C} \cdot \text{m}$ (2.038(8) D). Frequency shifts of the $KM = 0$ transitions which are second order in electric field were measured at

¹ In order to adequately describe the experimental procedures it is necessary to mention specifically the company that provided the chemical sample. This is not to be construed as an endorsement by NIST that this is the only company that could provide the sample.

TABLE I
Observed Microwave Transitions of $(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{CH}$

Transition	Normal species	$(\text{CF}_3)_3\text{C}-\text{C}^{13}\text{CH}$	$(\text{CF}_3)_3\text{C}-^{13}\text{CCH}$	$(\text{CF}_3)^{13}\text{C}-\text{CCH}$
7 ← 6	9672.296 ^a			
8 ← 7	11054.043	10921.278	11006.408	11053.218
9 ← 8	12435.793			
10 ← 9	13817.541			
11 ← 10	15199.282			
12 ← 11	16581.023			
13 ← 12	17962.765			

^a All frequencies are in MHz and the uncertainty in the measurements is 5 kHz.

fields between 240 and 400 V/cm and agreed with predictions ($\sigma = 2$ kHz) based on the analysis of the first-order frequency shifts of the higher KM components. In both cases, the effective plate spacing was determined using the $J = 1 \leftarrow 0$ rotational transition of OCS and the known electric dipole moment of OCS ($\mu_{\text{OCS}} = 2.3856 \times 10^{-30} \text{ C}\cdot\text{m}$ (0.71519 D) (5).

One transition of each of the three symmetric top, ^{13}C isotopomers was observed and these frequencies are also listed in Table I. No transitions arising from hot bands were observed. Using the standard Kraitchman substitution method, (6) the positions of these atoms were determined to be 2.9832 Å (C_1), 1.7800 Å (C_2), and 0.234 Å (C_3) from the center of mass. This gives r_s bond lengths of 1.2032 Å for the triple bond ($C_1\equiv C_2$) and 1.546 Å for the bond from the tetrahedral carbon to the acetylenic carbon (C_2-C_3).

Two pieces of data (the rotational constant and the position of the center of mass) constrain the remaining structural parameters. The molecules $(\text{CF}_3)_3\text{CH}$ and $(\text{CF}_3)_3\text{CI}$ have been studied by electron diffraction (7, 8). Both have CF bond lengths of 1.333(4) Å and FCF bond angles of 108°. Assuming these same values for $(\text{CF}_3)_3\text{CC}\equiv\text{CH}$, and fitting B and the center of mass, gives $R(C_3-C_4) = 1.549$ Å and $\angle C_2-C_3-C_4 = 106.47^\circ$, where C_4 is one of the off-axis carbon atoms. In this calculation, $R(C_1-H)$ was assumed to be 1.06 Å, the same as in methyl acetylene (9). Increasing $R(\text{CF})$ by 0.01 Å decreases $R(C_3-C_4)$ by 0.01 Å and increases the bond angle by 0.064°. The

TABLE II
Rotational Constants for $(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{CH}$

Isotopomer	B value (MHz)
Normal Species	
B	690.87916(4) ^a
D (Hz)	10.86(15)
$(\text{CF}_3)_3\text{C}-\text{C}^{13}\text{CH}$	682.5798
$(\text{CF}_3)_3\text{C}-^{13}\text{C}\equiv\text{CH}$	687.9004
$(\text{CF}_3)^{13}\text{C}-\text{C}\equiv\text{CH}$	690.8260

^a The numbers in parentheses represent 2σ error bars.

TABLE III
Structural Parameters for $(\text{CF}_3)_3\text{C}\equiv\text{CH}$

Parameter	Value ^a	Comment
$\text{C}_4\text{-F}$	1.333(4)	assumed from ED data ^b
$\angle \text{FC}_4\text{F}$	108.0°	assumed from ED data ^b
$\text{C}_1\text{-H}$	1.06	assumed from $\text{CH}_3\text{C}\equiv\text{CH}$ ^b
$\text{C}_1\equiv\text{C}_2$	1.2032	r_s (this work)
$\text{C}_2\text{-C}_3$	1.546	r_s (this work)
$\text{C}_3\text{-C}_4$	1.549	r_0 (this work)
$\angle \text{C}_2\text{-C}_3\text{-C}_4$	106.47°	r_0 (this work)

^a All bond lengths are in Angstroms and angles are in degrees.

^b See text for discussion.

present value of $R(\text{C}_3\text{-C}_4) = 1.549 \text{ \AA}$ can be compared with values of 1.537(3) \AA reported for $(\text{CF}_3)_3\text{CH}$ and 1.5444(15) \AA for $(\text{CF}_3)_3\text{Cl}$. The C-C-H bond angle in $(\text{CF}_3)_3\text{CH}$ is 105.8(3)° and $\angle \text{C-C-I} = 107.3(10)^\circ$ in $(\text{CF}_3)_3\text{Cl}$. The steric repulsion of the three $-\text{CF}_3$ groups is evident in the bond angles, and the small decrease in angle on going from I to CCH to H as the fourth substituent on the central carbon atom is consistent with decreasing size of the substituent group. Overall, the agreement of the present structure with the electron diffraction results of similar species is excellent. The structural parameters are summarized in Table III.

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