J. Phys. Chem. A **2002,** *106,* 3749−3753

Microwave Spectra of Four New Perfluoromethyl Polyyne Chains: Trifluoropentadiyne, $CF_3-C\equiv C-C\equiv C-H$, Trifluoroheptatriyne, $CF_3-C\equiv C-C\equiv C-C\equiv C-H$, Tetrafluoropentadiyne, $CF_3-C\equiv C-C\equiv C-F$, and Trifluoromethylcyanoacetylene, $CF_3-C\equiv C-C\equiv N$

Lu Kang and Stewart E. Novick*

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459

Received: November 8, 2001; In Final Form: January 29, 2002

Four fluoromethyl polyynes, 5,5,5-trifluoro-1,3-pentadiyne, $CF_3-C\equiv C-C\equiv C-H$, 7,7,7-trifluoro-1,3,5-heptatriyne, $CF_3-C\equiv C-C\equiv C-C\equiv C-H$, 1,5,5,5-tetrafluoro-1,3-pentadiyne, $CF_3-C\equiv C-C\equiv C-F$, and 4,4,4-trifluoro-1-nitrile-2-butyne, $CF_3-C\equiv C-C\equiv N$, were studied by pulsed-jet Fabry Perot Fourier transform microwave spectroscopy. The molecules were produced by pulsed high voltage discharges of dilute mixtures of precursor gases such as trifluoropropyne in an argon carrier pulsed jet. The carbon-13 and deuterium substituted isotopomers of trifluoropentadiyne were studied, and the molecular structure was determined.

Introduction

Highly unsaturated long chain hydrocarbons, both closed-shell species and radicals, make up the majority of the molecules detected in the interstellar medium.[1,2] These molecules have been identified, in the most part, by radio telescopes which operate in the microwave and millimeter regions of the spectrum. Such work is made possible by previous laboratory microwave spectroscopic studies of the likely interstellar molecules.[3] A recent example is the laboratory study of the rotational spectra of a series methylpolyynes, methylcyanopolyynes, cyanopolyynes, and isocyanopolyynes[4] which was performed, at least in part, to provide the radio astronomers with a list of frequencies (or equivalently, spectroscopic constants) for future astronomical searches. Thus, for example, the microwave spectroscopy of methylpolyacetylenes such as 1,3,5-heptatriyne, $CH_3-(C\equiv C)_3-H$, and its isoelectronic nitrile analogue, $CH_3-(C\equiv C)_2-C\equiv N$ are well studied both spectroscopically[5−7] and through ab initio calculations.[8]

A related series of molecules, for which only the shortest members of the series have been studied, are the fluorinated polyynes and cyanopolyynes. Trifluoropropyne,[9−14] $CF_3C\equiv CH$, trifluoroacetonitrile,[15−19] CF_3CN, and tetrafluoropropyne,[20] $CF_3C\equiv CF$, have been investigated by microwave spectroscopy in the ground vibrational state, and their structures have been determined. In these studies, it was found that, in contrast to expectations, the bond lengths, particularly that of the carbon−carbon triple bond, were not affected by the proximity of the electronegative fluorines to the extent predicted by theory.

In preparation for our microwave spectroscopic study of the hyperfine structure of conjugated fluorinated radicals such as $\bullet CF_2C\equiv CH$, we prepared gas samples containing trifluoromethylacetylene which were excited with a pulsed high voltage discharge. In addition to the expected radical, longer perfluoromethyl polyyne chain molecules were produced that have not been studied in the ground state with high-resolution spectroscopy. They are (**1**) $CF_3-C\equiv C-C\equiv CH$, 5,5,5-trifluoro-1,3-pentadiyne; (**2**) $CF_3-C\equiv C-C\equiv C-C\equiv CH$, 7,7,7-trifluoro-1,3,5-heptatriyne; (**3**) $CF_3-C\equiv C-C\equiv CF$, 1,5,5,5-tetrafluoro-1,3-pentadiyne; and (**4**) $CF_3-C\equiv C-C\equiv N$, 4,4,4-trifluoro-1-nitrile-2-butyne, also referred to as trifluoromethylcyanoacetylene.

Photoelectron spectra of the tetrafluoropentadiyne, (**3**),[21] and of the trifluorobutynenitrile, (**4**),[22] produced in a discharge, have been described, but no spectroscopic studies of **1** or **2** have been reported. We report here the microwave spectroscopic study of molecules **1**−**4**. The structure of **1**, trifluoropentadiyne, is determined from the moments of inertia of the parent, the deuterated, and each of the single-substituted carbon-13 isotopomers in natural abundance.

Experimental Section

The microwave spectra of the four fluorinated methyl acetylenes, **1**−**4**, were recorded using a Fabry−Perot pulsed-jet Fourier transform microwave spectrometer which has been described elsewhere.[23] Many modifications of the spectrometer have been made since that initial publication including coaxial expansion of the gas with the cavity axis for increased sensitivity and resolution, changes in the microwave circuitry for decrease in the microwave noise, and automatic scanning for ease of use.

In these experiments, a pulsed high voltage of typically 1000 V is applied between electrodes separated by 1 cm immediately following the pulsed gas valve whose nozzle diameter is typically 0.8 mm. The resulting plasma discharge with a current of typically 20 mA serves to "synthesize" the extended chains from smaller pieces. The precursor gas is a 1% mixture of two or three gases in a carrier gas of argon or neon with a total pressure of approximately 1 atm. The resultant mixture of precursors and products are expanded into the high *Q* Fabry−Perot microwave cavity which is tunable between 5 and 26.5 GHz. A microwave pulse is timed to coincide with the arrival of the gas pulse in the center of the microwave cavity. If a molecular transition lies within the ~500 kHz bandwidth of the microwave pulse/cavity combination, a macroscopic polarization is induced in the molecules. The free induction decay of this polarization is collected and averaged over multiple pulses and is Fourier transformed to yield the spectrum of the transition. The free induction decay was digitized at 100 ns per

---

* To whom correspondence should be addressed.

10.1021/jp0141068 CCC: $22.00

point for 4096 points, giving a discrete Fourier transform with a point every 2.44 kHz. With this, we can estimate peak centers, on most transitions, to within 1 kHz.

The precursor gas mixtures used for production of the four species varied slightly. For the production of (**1**) $CF_3-C\equiv C-C\equiv CH$, a mixture of 0.5% $CF_3C\equiv CH$ + 0.5% $HC\equiv CH$ in argon or neon was used. For the deuterated isotopomer, 0.2% $DC\equiv CD$ was substituted for the normal acetylene. For the production of (**2**) $CF_3-C\equiv C-C\equiv C-C\equiv CH$, a mixture of 0.5% $CF_3C\equiv CH$ + 0.5% $HC\equiv CH$ in argon or neon was used. For the production of (**3**) $CF_3-C\equiv C-C\equiv CF$, a mixture of 0.5% $CF_3C\equiv CH$ + 0.5% $HC\equiv CH$ + 0.5% CF_3H in argon or neon was used. For the production of (**4**) $CF_3-C\equiv C-C\equiv N$, a mixture of 0.5% $CF_3C\equiv CH$ + 0.5% $HC\equiv CH$ + 0.5% CH_3N in argon or neon was used.

The discharge which "synthesizes" these molecules is created using high voltage electrodes placed immediately after the pulsed nozzle. These electrodes and the insulated cup which holds them in place fits inside a hole bored in one of the mirrors that constitute the tuned microwave cavity. The upstream electrode is held at −1000 V; 1 cm downstream is the ground electrode. We always make the downstream electrode the ground to help minimize sparking to the grounded mirror. The discharge voltage pulse is timed to coincide with the gas mixture exiting the pulsed nozzle. We have found that the sign of the voltage of the upstream electrode is critical in the formation of the discharge related species. At least part of the energy of the plasma is transferred to the inert gas (the color of the discharge is blue for argon and orange for neon). It is likely that the collisions of the rare gas ions with the molecules result in the molecular fragmentation that precedes molecular buildup. In the case of the upstream electrode being negative, the Ar^+ ions experience an electrical force pulling them upstream against the direction of the downstream jet flow. This results in an increased number of energetic collisions between the Ar^+ ions and organic precursors of the radicals. It has been reported that having a *positive* upstream voltage is efficacious in the production of radicals and ions.[24] We have found that the sign of the voltage of the upstream electrode is critical and dependent upon the species we are attempting to produce. For example, the production of the HCCCO radical from an acrolein (CH_2-CHCHO)/Ar discharge is optimized with +600 V on the electrode; production of HCCCN from CH_2CHCN/Ar was about the same with both signs; the perfluoro compounds of the present experiment (and their all-hydrogen analogues) all optimize with the *negative* voltage upstream. In fact, we could not detect any signal in the present experiment when the voltage sign was switched. We note that the discharge with the positive upstream voltage (ion flow *with* the jet flow) is more intense and easier to strike as the electrodes get sooty.

For a carbon-13 isotopomer of $CF_3-C\equiv C-C\equiv C-H$, detected in natural abundance, a typical molecular transition reached a signal-to-noise-ratio of 5/1 in about 1000 gas pulses, which at 3 pulses/s amounts to an averaging time of about 5 min per transition. Such a transition is shown in Figure 1.

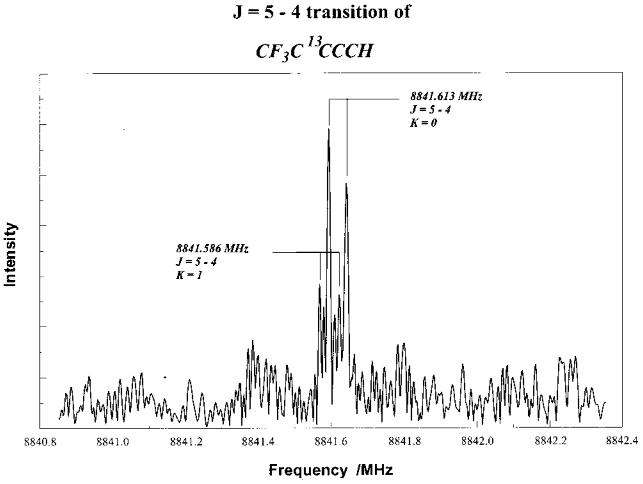

Figure 1. $J = 5-4$, K = 0 and K = 1 microwave transition of $CF_3-C\equiv {}^{13}C-C\equiv C-H$ in natural abundance. The spectrum required 1000 microwave/gas pulses and took 5.5 min to accumulate.

TABLE 1: Spectroscopic Constants of $CF_3-C\equiv C-C\equiv C-H$, $CF_3-C\equiv C-C\equiv C-C\equiv C-H$, $CF_3-C\equiv C-C\equiv C-F$, and $CF_3-C\equiv C-C\equiv N$[a]

	B/MHz	D_J/kHz	D_{JK}[b]/kHz
CF_3CCCCH	887.57431(4)	0.0175(2)	2.499(2)
$CF_3CCC^{13}CH$	862.69511(4)	0.0164(3)	2.39(3)
$CF_3CC^{13}CCH$	875.11021(4)	0.0163(2)	2.44(1)
$CF_3C^{13}CCCH$	884.16204(5)	0.0161(3)	2.55(3)
CF_3 13CCCCH	887.46051(9)	0.0163(5)	2.49(6)
$^{13}CF_3CCCCH$	885.43963(6)	0.0158(3)	2.59(4)
CF_3CCCCD	848.60969(3)	0.0145(2)	2.375(7)
$CF_3CCCCCCH$	379.57154(4)	0.00215(8)	0.79(2)
CF_3CCCCF	499.09390(3)	0.0044(1)	1.145(4)
CF_3CCCN[c]	885.94615(6)	0.0188(5)	

[a] The number in parentheses is the one standard deviation error of the constant from the least-squares fit. [b] D_{JK} was not measured for the nitrile, as only $K = 0$ transitions were recorded. [c] For this molecule, an additional spectroscopic constant was measured, the nuclear quadrupole coupling constant of the nitrogen nucleus projected along the *a* axis. It is $\chi_{aa} = -4.40(4)$ MHz.

Results

Microwave Spectra. Frequencies and assignments of the various isotopomers of $CF_3-C\equiv C-C\equiv CH$, trifluoropentadiyne, are presented in Table 1S, those of the normal isotopomers of $CF_3-C\equiv C-C\equiv C-C\equiv CH$, trifluoroheptatriyne, in Table 2S, of $CF_3-C\equiv C-C\equiv CF$, tetrafluoropentadiyne, in Table 3S, and of $CF_3-C\equiv C-C\equiv N$, trifluorobutynenitrile in Table 4S. These four tables are Supporting Information published in the Web edition of this journal. The transitions of the first three molecules were fit with a simple rigid rotor plus centrifugal distortion energy expression for a symmetric top

$$E = BJ(J+1) - D_J[J(J+1)]^2 - D_{JK}J(J+1)K^2$$

For the nitrile, a hyperfine term involving the nuclear quadrupole coupling constant for the spin-1 nitrogen nucleus, χ_{aa}, must be added

$$E_Q = \chi_{aa}\left[\frac{3K^2}{J(J+1)} - 1\right]f(I,J,F)$$

where $f(I,J,F)$ is the Casimir function[25] and F is the total angular momentum quantum number. The total angular momentum is the sum of the rotational angular momentum and the spin angular momentum of the nitrogen nucleus, $\mathbf{F} = \mathbf{J} + \mathbf{I}$. Only $K = 0$ transitions were detected for the trifluorobutynenitrile; thus, the D_{JK} constant was not measured for this molecule, and the formula for E_Q is simplified. The spectroscopic constants of the four molecules studied are presented in Table 1.

Molecular Structure. Of the four molecules studied, only (**1**), $CF_3-C\equiv C-C\equiv C-H$, trifluoropentadiyne, gave transition signals intense enough to allow observation of the transitions of the carbon-13 substituted isotopomers in natural abundance. (See Figure 1).

TABLE 2: r_s Structure of $F_3C_{(5)}-C_{(4)}\equiv C_{(3)}-C_{(2)}\equiv C_{(1)}-H$ and Related Molecules[a]

	$CF_3-C\equiv C-C\equiv C-H$[b]	$CF_3-C\equiv C-H$[c]	$CH_3-C\equiv C-C\equiv C-H$[d]
$r(C_1-H)$	1.0563(8)	1.0510(17)	1.055(1)
$r(C_2\equiv C_1)$	1.2075(6)	1.2012(8)	1.209(1)
$r(C_3-C_2)$	1.3689(11)		1.375(4)
$r(C_4\equiv C_3)$	1.2153(56)		1.208(4)
$r(C_5-C_4)$	1.4455(57)	1.4742(45)	1.456(3)
$r(F-C_5)$	1.3413(21)	1.3372(22)	1.105(1)
$\angle(F-C_5-F)$	107.20(8)°	108.27(20)°	108.58(5)°

[a] Distances are in angstroms; angles are in degrees. The numbers in parentheses are the estimated errors of the substitutional method (see text). [b] This work. [c] Reference 13. Because there are two fewer carbon atoms in trifluoromethylacetylene than in the other two molecules in the table, the numbering scheme is not a perfect match. $F_3C_{(5)}C_{(4or2)}\equiv C_{(1)}H$ is used. [d] Reference 30. $r(F-C_5)$ is to be read as $r(H-C_5)$, and $\angle(F-C_5-F)$ is to be read as $\angle(H-C_5-H)$ for methyldiacetylene.

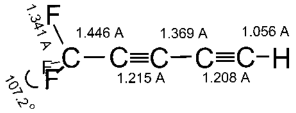

Figure 2. r_s structure of 5,5,5-trifluoro-1,3-pentadiyne.

We present a complete experimental determination of the structure of 5,5,5-trifluoro-1,3-pentadiyne. We have measured the rotational constants (essentially the inverses of the moments of inertia) of seven isotopomers of trifluoropentadiyne: the normal isotopomer, five singly substituted carbon-13 isotopomers, and the deuterated isotopomer. These rotational constants are presented in Table 1. Kraitchman's equations[26,27] were solved to give the *substitution*, or r_s, structure of the molecule which is, in general, closer to the equilibrium structure than is the average, or r_0, structure in which all of the isotopomer's moments of inertia would be simultaneously fit to a single best structure. In the r_s structure calculation, once the normal isotopomer's moment of inertia is measured, each measured isotopically substituted moment of inertia gives a coordinate for that substituted atom. Because the molecule is a symmetric top, we set the *b* and *c* coordinates of the carbon atoms and the hydrogen atom to be zero; the *a* inertial axis is the symmetry axis. Thus in $F_3C_{(5)}-C_{(4)}\equiv C_{(3)}-C_{(2)}\equiv C_{(1)}-H$, we can determine the *a* coordinate of the five carbon atoms and the hydrogen atom and thus all of the CC bond lengths and the CH bond length. The fluorine atom positions were determined by fitting their coordinates to the first and second moment equations for the normal isotopomer, $0 = \sum m_i a_i$ and $I_b = \sum m_i(a_i^2 + c_i^2)$. Thus we have fit seven structural parameters, six bond lengths, and one angle, from seven moments of inertia. With the number of unknowns equal to the number of equations, there is no independent check on the fitting procedure. Indeed, when we use the r_0 calculational procedure for these seven structural parameters, we obtain identical results for the bond lengths and the CFC angle. The errors from the carbon atom and deuterium atom r_s coordinates are used to calculate the errors for the CF bond length and the CFC angle with the use of standard error propagation. Errors in the substitution structure arise when the substituted atom is near the center of mass of the molecule. Costain has empirically estimated this contribution to the error to be $\delta r \approx (0.0012\ \text{Å}^2)/|r|$.[28] In our calculations we use 0.0015 Å^2 for heavy atoms and 0.003 Å^2 for the hydrogen atom as the conversion factor for this error.[29] The resulting r_s structure of trifluoropentadiyne is presented in Table 2 and shown in Figure 2.

Discussion

For $CF_3-C\equiv C-H$, ab initio calculations at the SCF level with a double-ζ basis set augmented by polarization functions on carbon[30] predicted a very short C≡C bond length of 1.185 Å, which was not found experimentally. The experimental distance was found to be shortened, but by 0.007 Å to 1.201 Å[13], from the 1.208 Å CC triple bond length of $CH_3-C\equiv C-H$.[20]

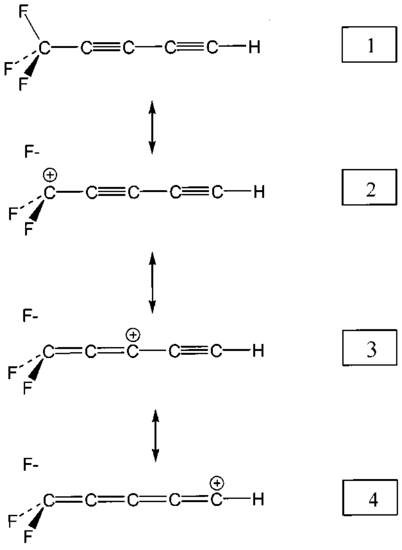

Figure 3. Resonance structures of 5,5,5-trifluoro-1,3-pentadiyne. The relative importance of these resonance structures to the bonding of the molecule is #1 > #2 > #3 > #4.

In the present case of $CF_3-C\equiv C-C\equiv C-H$, the situation is reversed, in that the CC triple bond closest to the trifluoromethyl group is *lengthened* by 0.007 Å to 1.215 Å from the corresponding bond length of 1.208 Å in $CH_3-C\equiv C-C\equiv C-H$.[31,32] The various distances and angles for CF_3C_4H, CF_3C_2H, and CH_3C_4H are presented in Table 2. The magnitude of differences in the distances between corresponding bond lengths in CF_3C_4H verses those of CH_3C_4H is greatest near the CF_3- end of the molecule. The differences of the bond lengths of CF_3C_4H minus those of CH_3C_4H are −0.010, +0.007, −0.006, −0.001, and +0.001 Å as we march from $CF_3-CCCCH$ through $CF_3C\equiv CCCH$, $CF_3CC-CCH$, and $CF_3CCC\equiv CH$ to $CF_3CCCC-H$.

This shortening of the CC single bond and the lengthening of the CC triple bond nearest the CF_3 group can be understood qualitatively in terms of the electron withdrawing ability of the fluorines. Figure 3 shows four resonance structures for trifluoromethylpentadiyne. Resonance structure #1 is, of course, the main contribution to the electronic structure of the molecule. However, because fluorine is highly electronegative and thus capable of electron withdrawing, resonance structures #2−4, in which one of the fluorine atoms has a full negative charge make some contribution to the total electronic structure. (The relative importance of the resonance structures is #1 > #2 > #3 > #4). Resonances #2−4, involving interactions between σ and π bonds, are referred to as involving "hyperconjugation". Resonance structures #3 and #4 both replace the $F_3C{-}C{\equiv}C$ end of the molecule with F^- $F_2C{=}C{=}C$. Thus, if we include these two resonance structures in the description of the bonding of the molecule, the single bond has some double bond character, thus shortening it, and the triple bond has some double bond character, thus lengthening it, as observed experimentally. Resonance structure #3 is more important than #4 because opposite charges are closer together in #3 (it takes energy to separate opposite charges); thus, the shortening/lengthening occurs in the two bonds near the CF_3 end of the molecule.

The subtle effect upon the electronic structure of the methylacetylenes upon fluorination of the methyl group can also be observed in $CF_3{-}C{\equiv}C{-}C{\equiv}N$, trifluoromethylcyanoacetylene. Here we have measured the nuclear quadrupole coupling constant for the spin-1 nitrogen nucleus, χ_{aa}, to be −4.40(4) MHz. This is larger in magnitude than values of this constant for methylcyanide,[33] CH_3CN (−4.214(14) MHz); for methylcyanoacetylene,[34] $CH_3C{\equiv}CCN$, (−4.0(2) MHz); and for methylcyanodiacetylene,[7] $CH_3C{\equiv}C{-}C{\equiv}CCN$, (−4.25(3) MHz). [Methylcyanoacetylene is the closest analogue of CF_3CCCN, but its value of χ_{aa} is the least well measured; the correct value is most probably −4.2 MHz as in the shorter and the longer chain version.] The nuclear quadrupole coupling constant is proportional to the product of quadrupole moment of the nucleus in question and the electric field gradient at that nucleus caused by all of the positive and negative charges of the molecule but most especially by the electrons nearest the nucleus. Thus, a qualitative understanding of the increase in the magnitude of $\chi_{aa}(^{14}N)$, from 4.2 to 4.4 MHz upon fluorination of CH_3CCCN to CF_3CCCN, can be obtained from the electron distribution surrounding the nitrogen nucleus. The relevant resonance structures are those analogous to #1 and #4 of Figure 3: $F_3C{-}C{\equiv}C{-}C{\equiv}N \leftrightarrow F^-\ F_2C{=}C{=}C{=}C{=}N^{\oplus}$. Although resonance structure #4 is the least important, subtle electronic variations which seem not to affect bond lengths can have a major effect upon electric field gradients and thus upon nuclear quadrupole coupling constants.[13]

Townes and Schawlow[25] give a simple correlation between electric field gradients, q, and electron bonding. Assume that the p_σ bonding orbital is fractionally s-hybridized by an amount f_s in both resonance structures #1

$$\equiv\!N\!: \qquad (\#1)$$

and in resonance #4

$$\underset{\oplus}{=\!N\!:} \qquad (\#4)$$

then the nonbonding lone-pair electrons must be $(1 - f_s)$ s character and f_s p_σ character. Because s electrons are spherically symmetric, only p electrons contribute to a field gradient along the molecular axis. Because of their different orientations, electrons in the p_π orbitals have field gradients, q_1, along the a axis that are $-{}^1/_2$ of the field gradients because of the electrons in the p_σ orbitals, q_0; that is, $q_1 = -{}^1/_2 q_0$.[25,35] Resonance structure #1 has a field gradient at the nitrogen nucleus of

$$q(\#1) = (1 - f_s)q_0 + 2q_1 + 2f_s q_0 = f_s q_0$$

where the first term is due to the bonding p_σ electron, the second term is due to to the two bonding p_π electrons, and the third term is due to the two nonbonding lone pair electrons. A reasonable value for f_s is 0.45.[25] Resonance structure #4 has a field gradient at the nitrogen nucleus of

$$q(\#4) = (1 - f_s)q_0 + q_1 + 2f_s q_0 = (f_s + {}^1/_2)q_0$$

where the terms are in the same order as above; there is only one bonding p_π electron for resonance structure #4. The difference, $q(\#4) - q(\#1)$, is equal to ${}^1/_2 q_0$.[36] Thus, the slight contribution of resonance #4 to the electronic structure of CF_3-CCCN rationalizes the increase of the magnitude of $\chi_{aa}(^{14}N)$ in CF_3CCCN over that in CH_3CCCN.

Summary

We have studied, by microwave spectroscopy, four related fluoromethyl acetylenes: CF_3C_4H, CF_3C_6H, CF_3C_4F, and CF_3C_2-CN. The molecular structure of the first of these, $CF_3{-}C{\equiv}C{-}C{\equiv}C{-}H$, was determined and the bond lengths discussed in terms of the electron withdrawing capability of the electronegative fluorines. The same analysis was used to understand the nuclear quadrupole coupling constant of the nitrogen in the nitrile, $CF_3{-}C{\equiv}C{-}C{\equiv}N$.

Acknowledgment. We thank Jens-Uwe Grabow for supplying us with the new version of his Windows-based software *ftmw++* which now operates the spectrometer and for all his help in installing and debugging this program. This work was supported by the National Science Foundation.

Supporting Information Available: The complete set of the observed transitions, assignments, and the deviations from the predicted frequencies (obs. − calcd) for the four molecules discussed in this paper are presented in Tables 1S−4S. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) A list of the molecules detected in the dense interstellar clouds and other astronomical sources can be found at http://www.cv.nrao.edu/~awootten/allmols.html.

(2) Allamandola, L. J.; Hudgins, D. M.; Bauschlicher, C. W., Jr.; Langhoff, S. R. *Astron. Astrophys.* **1999**, *352*, 659.

(3) Winnewisser, G.; Herbst, E.; Ungerechts, H. In *Spectroscopy of the Earth's Atmosphere and Interstellar Medium*; Rao, K. N., Weber, A., Eds.; Academic Press: New York, 1992; p 423.

(4) McCarthy, M. C.; Chen, W.; Travers, M. J.; Thaddeus, P. *Astrophys. J. Supp. Ser.* **2000**, *129*, 611.

(5) Alexander, A. J.; Kroto, H. W.; Maier, M.; Walton, D. R. M. *J. Mol. Spectrosc.* **1978**, *70*, 84.

(6) Bester, M.; Yamada, K.; Winnewisser, G.; Joentgen, W.; Altenbach, H. J.; Vogel, E. *Astron. Astrophys.* **1984**, *137*, L20.

(7) Chen, W.; Grabow, J.-U.; Travers, M. J.; Munrow, M. R.; Novick, S. E.; McCarthy, M. C.; Thaddeus, P. *J. Mol. Spectrosc.* **1998**, *192*, 1.

(8) Arnau, A.; Tunon, I.; Andres, J.; Silla, E. *Chem. Phys. Lett.* **1990**, *166*, 54.

(9) Anderson, W. E.; Trambarulo, R,; Sheridan, J.; Gordy, W. *Phys. Rev.* **1951**, *82*, 58.

(10) Shoolery, J. N.; Shulman, R. G.; Sheehan, W. F.; Schomaker, V.; Yost, D. *J. Chem Phys.* **1951**, *19*, 1364.

(11) Mills, I. M. *Mol. Phys.* **1969**, *16*, 345.

(12) Kasten, W.; Dreizler, H. *Z. Naturforsch. A* **1984**, *39*, 1003.

(13) Cox, A. P.; Ellis, M. C.; Legon, A. C.; Wallwork, A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2937.

(14) Harder, H.; Gerke, C.; Maeder, H.; Cosleou, J.; Bocquet, R.; Demaison, J.; Papousek, D.; Sarka, K. *J. Mol. Spectrosc.* **1994**, *167*, 24.

(15) Sheridan, J.; Gordy, W. *J. Chem. Phys.* **1952**, *20*, 591.

(16) Thomas, L. F.; Heeks, J. S.; Sheridan, J. *Z. Electrochim.* **1957**, *61*, 935.

(17) Foreman, P. B.; Chien, K. R.; Williams, J. R.; Kukolich, S. G. *J. Mol. Spectrosc.* **1974**, *52*, 251.

(18) Kasten, W.; Dreizler, H.; Job, B. E.; Sheridan, J. *Z. Naturforsch. A* **1983**, *38*, 1015.

(19) Friedrich, A.; Gerke, C.; Harder, H.; Maeder, H.; Cosleou, J.; Wlodarczak, G.; Demaison, J. *Mol. Phys.* **1997**, *91*, 697.

(20) Cox, A. P.; Ellis, M. C.; Summers, T. D.; Sheridan, J. *J. Chem Soc. Faraday. Trans.* **1992**, *88*, 1079.

(21) Bieri, G.; Heilbronner, E.; Stadelmann, J.-P.; Vogt, J.; von Niessen, W. *J. Am. Chem. Soc.* **1977**, *99*, 6832.

(22) Bieri, G.; Heilbronner, E.; Hornung, V.; Kloster-Jensen, E,.; Maier, J. P.; Thommen, F.; von Niessen, W. *Chem. Phys.* **1979**, *36*, 1.

(23) Hight Walker, A. R.; Chen, W.; Novick, S. E.; Bean, B. D.; Marshall, M. D. *J. Chem. Phys.* **1995**, *102*, 7298.

(24) Anderson, D. T.; Davis, S.; Zwier, T. S.; Nesbitt, D. J. *Chem. Phys. Lett.* **1996**, *258*, 207. David Nesbitt, private communication.

(25) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; McGraw-Hill: New York, 1955.

(26) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17.

(27) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; Wiley: New York, 1984; Chapter 13.

(28) Costain, C. C. *Trans. Am. Crystallogr. Assoc.* **1966**, *2*, 157.

(29) van Eijck, B. P. *J. Mol. Spectrosc.* **1982**, *91*, 348.

(30) Dixon, D. A.; Smart, B. S. *J. Phys. Chem.* **1989**, *93*, 7772.

(31) Nielsen, C. J.; Saebo, S. *Acta Chem. Scan. A* **1983**, *37*, 267.

(32) The error estimates in the positions of the atoms in the r_s structure calculation are an order of magnitude greater than the errors in the rotational constants would imply. This larger error is partially an attempt to estimate how the r_s structure differs from the hypothetical r_e structure (see, for example, ref 29). Our quoted bond length difference of 0.007 Å, being a direct comparison of r_s derived bond lengths, is meaningful.

(33) Kemp, M. K.; Pochan, J. M.; Flygare, W. H. *J. Chem. Phys.* **1967**, *71*, 765.

(34) Bester, M.; Tanimoto, M.; Vowinkel, B.; Winnewisser, G.; Yamada, K. *Z. Naturforsch. A* **1983**, *38*, 64.

(35) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; Wiley: New York, 1984; Chapter 14.

(36) Because resonance structure #4 nominally involves a positive ion, there is compression of all of the orbitals and, thus, an additional increase in the field gradient, which involves an integral of $1/r^3$. This increase is estimated to be a factor of 1.25 (ref 25, pg 239).