Rotational spectrum and carbon-13 hyperfine structure of the C\textsubscript{3}H, C\textsubscript{5}H, C\textsubscript{6}H, and C\textsubscript{7}H radicals

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By means of Fourier transform microwave spectroscopy of a supersonic molecular beam, we have detected the singly substituted carbon-13 isotopic species of C\textsubscript{3}H, C\textsubscript{5}H, and C\textsubscript{7}H. Hyperfine structure in the rotational transitions of the lowest-energy fine structure component (\( ^2\Pi_{1/2} \)) for C\textsubscript{3}H and C\textsubscript{5}H, and \( ^2\Pi_{3/2} \) for C\textsubscript{6}H) of each species was measured between 6 and 22 GHz, and precise rotational, centrifugal distortion, \( \Lambda \)-doubling, and \(^{13}\text{C} \) hyperfine coupling constants were determined. In addition, resolved hyperfine structure in the lowest rotational transition (\( J=3/2 \rightarrow 1/2 \)) of the three \(^{13}\text{C} \) isotopic species of C\textsubscript{3}H was measured by the same technique. By combining the centimeter-wave measurements here with previous millimeter-wave data, a complete set of \(^{13}\text{C} \) hyperfine coupling constants were derived to high precision for each isotopic species. Experimental structures (\( r_0 \)) have been determined for C\textsubscript{3}H and the two longer carbon-chain radicals, and these are found to be in good agreement with the predictions of high-level coupled-cluster calculations. C\textsubscript{3}H, C\textsubscript{5}H, and C\textsubscript{7}H exhibit a clear alternation in the magnitude and sign of the \(^{13}\text{C} \) hyperfine coupling constants along the carbon-chain backbone. Because the electron spin density is nominally zero at the central carbon atom of C\textsubscript{3}H, C\textsubscript{5}H, and C\textsubscript{7}H, and at alternating sets of carbon atoms of C\textsubscript{4}H and C\textsubscript{6}H, owing to spin polarization, almost all of the \(^{13}\text{C} \) coupling constants at these atoms are small in magnitude and negative in sign. Spin-polarization effects are known to be important for the Fermi-contact (\( b_f \)) term, but prior to the work here they have generally been neglected for the hyperfine terms \( a, c, \) and \( d \). © 2005 American Institute of Physics.

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I. INTRODUCTION

The hydrocarbon radicals C\textsubscript{4}H are important reactive intermediates in combustion processes and in interstellar chemistry. Reactions of these carbon chains with acetylene are believed to be the dominant production mechanism for polyacetylenes and soot in nearly all hydrocarbon fuels at high temperature,\(^1 \) and they are thought to play a key role in the synthesis of larger molecules in space. A total of eight radicals, from CH to C\textsubscript{7}H, have now been detected in space with large radio telescopes,\(^2 \) the smaller ones in many astronomical sources, the larger ones in two particularly rich ones: the expanding envelope of the carbon-rich star IRC +10216, and the cold, dense molecular cloud TMC-1. In the laboratory, the rotational spectra of chains up to C\textsubscript{3}H have been detected by Fourier transform microwave (FTM) spectroscopy of a supersonic molecular beam,\(^3 \) and the optical spectra of chains up to C\textsubscript{10}H have been detected by laser-induced fluorescence,\(^4 \) cavity ringdown,\(^5,6 \) or resonant two-color two-photon photoionization spectroscopy.\(^7,8 \)

With the exception of C\textsubscript{2}H and C\textsubscript{6}H, it is now well established that the C\textsubscript{4}H radicals possess \( ^2\Pi \) ground states: those with an odd number of carbon atoms have regular spin-orbit splitting and a \( ^2\Pi_{1/2} \) ground state, while those with an even number have inverted spin-orbit splitting and a \( ^2\Pi_{3/2} \) ground state. All possess linear (or nearly linear) heavy atom backbones and substantial permanent electric dipole moments, making them good candidates for astronomical detection. In the expanding circumstellar shell of IRC+10216,\(^9 \) C\textsubscript{7}H is so conspicuous that its more abundant rare isotopic species have been detected. In the laboratory, isotopic studies of chains up to C\textsubscript{4}H have been undertaken at centimeter wavelengths by FTM spectroscopy,\(^10 \) at millimeter wavelengths by long-path absorption spectroscopy,\(^11-14 \) or by both techniques.

The molecular structures and chemical bonding of the C\textsubscript{4}H radicals are of theoretical interest because many properties of the electronic ground states of these molecules are sensitive to the level of theory and size of the basis set used in quantum chemical calculations. The energy ordering and separation between the low-lying \(^2\Sigma^+ \) and \(^2\Pi \) states has been the subject of several calculations,\(^15-18 \) but large variations in the lengths of individual C–C and C–H bonds have also been reported. At the RCCSD(T) level of theory, for example, the length of nearly all the C–C and C–H bonds from C\textsubscript{4}H to C\textsubscript{7}H decreases by \( \sim 0.03 \) Å when the basis set is improved from cc-pVDZ to cc-pVTZ.\(^19 \) The bonding for each radical is most closely approximated as acetylenic, but many bonds vary in length from those of standard single and triple C–C bonds. Because geometries have proven to be a computational challenge, experimental determinations of the structure of C\textsubscript{4}H and longer chains serve as a sensitive check on the theoretical calculations.
The $^{13}$C magnetic hyperfine coupling constants have also been determined to high accuracy at each carbon atom in $\text{C}_2\text{H}$, $\text{C}_3\text{H}$, and $\text{C}_4\text{H}$. For the odd-numbered radicals from $\text{C}_3\text{H}$ to $\text{C}_7\text{H}$, the hyperfine constants demonstrate that the unpaired electron is localized primarily at alternating carbon atoms starting at the terminal carbon of each chain; the spin density is largest there, and decreases smoothly as the distance from the terminal atom increases. Because the spin density is nominally zero at the central carbon atom of $\text{C}_2\text{H}$, $\text{C}_3\text{H}$, and $\text{C}_4\text{H}$, and at the other sets of alternating carbon atoms of $\text{C}_5\text{H}$ and $\text{C}_7\text{H}$, the $^{13}$C hyperfine constants are generally small and negative. The magnitude and sign of each hyperfine term can be explained by spin polarization, an effect previously invoked to explain the sign of only one term, the Fermi-contact coupling constant $b_F$.

II. EXPERIMENT

The same FTM spectrometer and discharge source used to produce $\text{C}_5\text{H}$ and still longer free radicals to $\text{C}_{13}\text{H}$ (Ref. 3) was employed in the present investigation. The spectrometer operates in the centimeter-wavelength band from 5 to 43 GHz and possesses a very sensitive microwave receiver which can be cooled together with the large confocal mirrors of the spectrometer to the temperature of liquid nitrogen. A small discharge to produce reactive molecules is struck in the throat of the supersonic nozzle through a stream of precursor gases heavily diluted in an inert buffer gas, followed by adiabatic expansion to about Mach 2 in a large vacuum chamber. The spectrometer is largely computer controlled; in spite of the small spectral coverage of each setting of the Fabry–Perot cavity (~0.2 MHz), automated scans covering wide frequencies and requiring many hours of total integration can be conducted with little or no oversight. For calibration, rotational lines of the normal isotopic species were routinely monitored. Because $\text{C}_5\text{H}$ possesses a large magnetic moment, care was taken to minimize the Earth’s magnetic field at the center of the Fabry-Perot cavity using three sets of mutually perpendicular Helmholtz coils; the residual of the Earth’s field was about 10–15 mG (about 3% of the zeroth-order field of 400 mG) over the active volume of the spectrometer, sufficiently small to allow resolution of closely spaced hyperfine structure (hfs)—but still large enough to broaden many of the lowest rotational transitions beyond the intrinsic instrumental linewidth of ~5 kHz that arises from time-of-flight of our highly divergent supersonic molecular beam. The optimal production conditions for the present chains are similar to those reported in earlier investigations of $\text{C}_5\text{H}$ and $\text{C}_7\text{H}$ by the same technique: a 1000 V low current discharge synchronized with a 200 µs long gas pulse. With a stagnation pressure of about 3 atm behind the pulsed valve of the nozzle, the gas flow was 8–20 cm$^3$/min at STP at the pulse rate of 6 Hz.

The lines of the singly substituted $^{13}$C isotopic species were observed in natural abundance, using acetylene (0.1%) heavily diluted in Ne for $\text{C}_3\text{H}$ and diacetylene (0.2%) in Ne for the three longer chains—mixtures which give the strongest lines of the normal species for each chain. For $\text{C}_5\text{H}$, acetylene produces stronger lines by almost a factor of 3 than

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**Fig. 1.** Experimental ($r_0$) structures of $\text{C}_2\text{H}$, $\text{C}_3\text{H}$, and $\text{C}_4\text{H}$ obtained by isotopic substitution. Bonds lengths are in angstroms and uncertainties (1σ) are in the units of the last significant digit. For $\text{C}_2\text{H}$, the C–H bond is anomalously short because of large amplitude motion of the $v_3$ mode (see Ref. 14). The bond order is only approximate as several different resonance structures contribute to the ground state.
An increase in the intensity of the $^{13}$C lines by a factor of 2 or more was readily achieved in two ways: (1) by adding $^{13}$C-enriched carbon monoxide (0.8%) to the mixture, to produce sixfold stronger lines of $^{13}$C-C$_2$H than those observed in natural abundance, about sixfold stronger lines of $^{13}$C-C$_2$H, and about twofold stronger lines of $^{13}$C-C$_2$H and C$_2$H; or (2) by adding a small amount (0.2%) of statistical carbon-13 HCCH (i.e., 25% HCCH, 50% $^1$H$^{13}$CCH, and 25% $^2$H$^{15}$C$^{13}$CH) to the mixture, to produce a sixfold enhancement of $^{13}$C-C$_2$H, and a threefold enhancement of $^{13}$C-H$_2$ and C$_2$H. The statistical mixture of carbon-13 HCCH was produced by the hydrolysis of $^{13}$C-enriched Li$_2$C$_2$ which was prepared by the NIH Stable Isotope Resource, Los Alamos National Laboratory. For speed and convenience, most of the measurements were made with one of the $^{13}$C enriched mixtures.

Under favorable conditions, the strongest hyperfine-split lines of the $^{13}$C species of C$_2$H and C$_2$H were observed with a signal-to-noise ratio of 20 in 2 or 3 min of integration, while considerable more time—about 20 min—was required to observe the same lines of C$_2$H at comparable signal-to-noise ratio. For C$_2$H, integration times of about 30 min were required to observe the lines of the six different $^{13}$C species with a signal-to-noise of 3, which with isotopic enrichment was increased to 10. With enrichment the line intensities of the singly substituted $^{13}$C species of each chain are nearly equal, indicating that in our discharge the carbon from either carbon monoxide or acetylene is randomly shuffled in the assembly of the longer chains. Sample lines of C$_2$H are shown in Fig. 2, and those of C$_2$H, C$_3$H, and C$_4$H in Fig. 3.

For the $^{13}$C isotopic species of C$_2$H, searches for the hfs of the $J=3/2 \rightarrow 1/2$ transition near 32 GHz were based on spectroscopic constants derived from the previous millimeter-wave study of Kanada et al. They determined all of the ground state hyperfine coupling constants for $^{13}$CCCH and CC$^{13}$CH, and all but the A-doubling term $d$ for C$_2^{13}$CH, taking into account the vibronic interaction between the $X^2\Pi$ and the low-lying $^2\Sigma^+$ state in the rotational analysis. For the hyperfine components with the strongest intensities, predictions from the millimeter-wave data alone were generally accurate to several megahertz, but for many of the weaker components these predictions were less accurate by a factor of three or more.

Searches for the $^{13}$C isotopic species of C$_2$H, C$_3$H, and C$_4$H were guided by ab initio calculations of Woon. Rotational constants were estimated by scaling the ab initio constants by the ratio of the experimental $B$ value to that calculated at the same level of theory for the normal species. Rotational transitions predicted in this way were accurate to within 0.1% for all three radicals. For all the singly substituted $^{13}$C lines, measured line frequencies typically agree with those predicted to within a few megahertz, so extensive frequency searches were unnecessary. The largest uncertainty originated from the $^{13}$C hfs which could not be well predicted a priori, and typically varied from a few megahertz to a few hundred kilohertz for different species.

![Diagram](http://jcp.aip.org/jcp/copyright.jsp)

**FIG. 2.** A portion of the $J=3/2 \rightarrow 1/2$ transition of $^{13}$CCCH showing two of the stronger hyperfine components near 32 GHz. The spectrum was recorded with a dilute mixture of acetylene (0.1%) and $^{13}$CO (0.8%) in Ne at an integration time of 5 min per MHz. The double-peaked line profile is instrumental in origin—the Doppler splitting that results when the Mach 2 axial molecular beam interacts with the standing wave in the confocal Fabry–Perot of the spectrometer. The two weak features displaced to slightly higher frequency from each strong line are denoted as "I" (images). These ghost features of the two strong lines are present in the observed spectrum because of incomplete suppression of the image band of the heterodyne receiver when the cavity quality factor is very low ($Q \sim 10^6$).

### III. SPECTROSCOPIC ANALYSIS

Rotational spectra were analyzed with a standard Hamiltonian for a linear $^2$II molecule with two nuclear spins, $^{13}$C and H magnetic hyperfine interactions, the coupling scheme

$$J = N + S, \quad F_j = J + I(\text{C}), \quad F = F_j + I(\text{H})$$

was adopted. For several $^{13}$C species of C$_2$H, a more natural choice for the coupling scheme would be $F_j = N + I(\text{C}), \quad F = F_j + S$, because the $^{13}$C hyperfine interaction is comparable or larger than the A-doubling, but the fitting program readily handles the large off-diagonal terms in the Hamiltonian when the coupling scheme in Eq. (1) is used, so, for uniformity, that was adopted in all cases.

#### A. Isotopic species of C$_3$H

Preliminary fits were performed for each isotopic species when the four or five strongest hyperfine components were measured at centimeter wavelengths. All but the rotational constant $B$, the A-doubling constant $p$, and one or two $^{13}$C coupling constants (typically $h_F$ and $c$) were constrained to the values derived from the millimeter-wave data. In these initial fits, an rms of $\leq 20$ kHz was typically achieved. New predictions were then generated on the basis of the refined constants, and searches for additional hyperfine components were undertaken, with most lines lying within a few hundred kilohertz of the predicted frequencies. At least 15 hyperfine
components, including many weaker $\Delta F_i \neq \Delta F$ transitions, were eventually measured for each species (see Table I). By-varying $B$, $p$, and the four $^{13}$C coupling constants in fits to the full set of FTM data, a rms comparable to the 5 kHz uncertainty in the line measurements was achieved.

After the FTM hfs was assigned, global fits which include previous millimeter-wave data were performed. The centimeter-wave lines were assigned frequency uncertainties of 5 kHz and the millimeter-wave lines in both the $X^2\Pi$ (Ref. 25) and $^3\Sigma$ states were assigned a uniform uncertainty of 40 kHz. Each hyperfine line was thus given a weight of roughly 65 relative to each of the 20–25 partially hyperfine-split millimeter-wave lines which range from $J = \frac{15}{2} - \frac{31}{2}$ in the $^2\Pi$ state and $N = 10 - 15$ in the $^3\Sigma$ state. The final hyperfine parameters derived from the global fits are nearly identical to those calculated from the initial fits,
and the global rms are comparable to those obtained from the millimeter-wave data alone. Tables II and III list the spectroscopic parameters determined from the global fit for each singly substituted $^{13}$C isotopic species of C$_3$H—the best summary of all the data at hand.

Compared to the ground state molecular constants of Kanada et al., $B$, $p$, and three of the four $^{13}$C coupling constants ($a$, $b_p$, and $c$) are more accurately determined by factors ranging from 10 to 30 for each isotopic species. The accuracy of the fourth hyperfine constant, the A-doubling term $d$, is improved by an even larger factor—nearly three orders of magnitude—for $^{13}$CCCH and CC$^{13}$CH, and has been determined for the first time here for C$^{13}$CCCH. In the low-lying $^2\Sigma$ state, the accuracy of $b_p$($^{13}$C) has also been improved by more than an order of magnitude.

### B. Isotopic species of C$_3$H, C$_2$H, and C$_2$H

The lower rotational transitions of C$_3$H and C$_2$H in its $X^2\Pi_{1/2}$ fine structure ladder and C$_2$H in its $X^2\Pi_{3/2}$ ladder are split into two components by $\Lambda$-doubling of order 2–5 MHz and then by $^{13}$C hfs, generally smaller by about a factor of 2 or 3; they are further split by hfs from the hydrogen nucleus, generally smaller by another factor of 2 or

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**TABLE I. Hyperfine-split lines in the $J=3/2 \rightarrow 1/2$ transition of isotopic C$_3$H.**

<table>
<thead>
<tr>
<th>Transition</th>
<th>$F_i'^2,F_i$</th>
<th>$F_i^2-F$</th>
<th>$e/f$</th>
<th>$^{13}$CCCH</th>
<th>C$^{13}$CH</th>
<th>CC$^{13}$CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$\rightarrow$0</td>
<td>3/2$\rightarrow$1/2</td>
<td>e</td>
<td>31 432 898</td>
<td>31 659 091</td>
<td>31 659 091</td>
<td></td>
</tr>
<tr>
<td>1$\rightarrow$1</td>
<td>3/2$\rightarrow$1/2</td>
<td>e</td>
<td>31 439 133</td>
<td>31 651 714</td>
<td>31 655 851</td>
<td></td>
</tr>
</tbody>
</table>

---

**TABLE II. Rotational, A-doubling, and centrifugal-distortion constants of isotopic C$_3$H.**

<table>
<thead>
<tr>
<th>Constant</th>
<th>$^{13}$CCCH</th>
<th>C$^{13}$CH</th>
<th>CC$^{13}$CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2\Pi$ ground state</td>
<td>A</td>
<td>432 433(7)</td>
<td>432 255(8)</td>
</tr>
<tr>
<td>B</td>
<td>10 755.838(10)</td>
<td>11 187.893(11)</td>
<td>10 842.562(8)</td>
</tr>
<tr>
<td>$^{10}D$</td>
<td>4.780(3)</td>
<td>5.110(3)</td>
<td>4.782(3)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$-52.17(17)$</td>
<td>$-50.44(17)$</td>
<td>$-46.67(15)$</td>
</tr>
<tr>
<td>$p$</td>
<td>$-7.013(7)$</td>
<td>$-7.437(7)$</td>
<td>$-7.881(6)$</td>
</tr>
<tr>
<td>$q$</td>
<td>$-11.881(17)$</td>
<td>$-12.860(18)$</td>
<td>$-12.336(14)$</td>
</tr>
</tbody>
</table>

**TABLE III. Hyperfine coupling constants of isotopic C$_3$H.**

<table>
<thead>
<tr>
<th>Isotopic species</th>
<th>$a$($^{13}$C)</th>
<th>$b_p$($^{13}$C)</th>
<th>$c$($^{13}$C)</th>
<th>$d$($^{13}$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2\Pi$ ground state</td>
<td>1$^{13}$CCCH</td>
<td>66.7(5)</td>
<td>32.6(3)</td>
<td>$-84.7(10)$</td>
</tr>
<tr>
<td>C$^{13}$CH</td>
<td>1.4(5)</td>
<td>$-46.3(3)$</td>
<td>19.9(3)</td>
<td>$-6.942(5)$</td>
</tr>
<tr>
<td>CC$^{13}$CH</td>
<td>43.6(5)</td>
<td>112.5(3)</td>
<td>$-64.8(10)$</td>
<td>90.054(4)</td>
</tr>
</tbody>
</table>

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**Note:** Units are in megahertz; uncertainties in parentheses are 1σ. Spectroscopic constants derived from data in Table I and millimeter-wave data in Ref. 14.
and two $^{13}$C hyperfine constants ($a$ and $b$) were required to reproduce roughly 32 measured lines for each isotopic species to better than 5 kHz. The spectroscopic constants obtained from the fits are given in Table V.

The present identifications are extremely secure: (i) the carriers of the lines assigned here to $C_3H$, $C_3H$, and $C_3H$ are almost certainly radicals, because their rotational transitions are separated in frequency by half-integer quantum numbers, and the lines exhibit the expected Zeeman effect (i.e., a fairly modest broadening for $C_3H$ and $C_3H$ owing to the small magnetic $g$ factor of a $^2\Sigma^1/2$ state, and significant broadening for $C_3H$ owing to the large magnetic $g$ factor of a $^1\Pi_3/2$ state) when a permanent magnet is brought near the molecular beam; (ii) the carriers of the observed lines exhibit additional splitting beyond that expected from the H nucleus alone in all of the assigned spectra, which is consistent with Hfs from the carbon-13 nucleus; and (iii) line intensities increase by the expected factor when enriched samples of $^{13}$C are used.

As a final check on the assignments, we note that the identifications are supported on spectroscopic grounds by the close agreement of $B$ with that estimated by scaling from the $ab$ initio geometries, and that the $\Lambda$-doubling constants ($p$ for $C_3H$ and $C_3H$, $q$ for $C_3H$) and the centrifugal distortion constants (for $C_3H$) for the isotopic species of a given chain, as required, are all very nearly the same (Table V). The constant $p$ of $C_3H$ and $C_3H$ in fact can be predicted $a$ priori to high accuracy by scaling from the normal isotopic species on the assumption of free precession. The constant $q$ of $C_3H$ is not as well predicted by the same means probably because the $^2\Sigma$ state is extremely low lying.\textsuperscript{15-18} For $^{12}$CCCCCH, $q = -1.527(3)$ MHz, i.e., about 5% larger than normal $C_3H$, implying that the spin-orbit constant $A_{so}$ may be slightly smaller than the assumed value, a difference which would change the best-fit $B$ value (Table V) by only a very small amount (0.015% or about 0.2 MHz).

We can also be highly certain that each set of lines is correctly assigned to the right isotopic species. The center of mass (c.m.) falls very close to the central carbon atom of $C_3H$ and $C_3H$ and the midpoint of the central C–C bond of $C_3H$. As for the cyanopolyne chains,\textsuperscript{27} most of the carbon-13 shifts here occur in tightly spaced pairs, corresponding to the two carbon atoms at about the same distance from the c.m. For the innermost carbon pairs, the difference in $B$ is not much larger than the uncertainty in the $a$ priori isotope shifts in $B$. Because the c.m. is displaced either from the central carbon atom or the midpoint of the central carbon-carbon bond towards the hydrogen atom, however, any possible ambiguity is easily resolved: the isotopic species with the higher $B$ in each pair can be assigned with confidence to the carbon atom which is closest to the hydrogen end of the chain.

### IV. STRUCTURAL DETERMINATIONS

For each radical chain, a structure was determined from a least-squares fit of all the bonds in the molecule to the measured rotational constants in Table V: i.e., those of all the rare isotopic species plus the normal. It was assumed that each molecule is strictly linear. Toward the terminal atoms
Table V. Molecular constants determined in the least-squares fit of isotopic C₃H, C₄H, and C₅H.

<table>
<thead>
<tr>
<th>Isotopic species</th>
<th>B</th>
<th>10⁹D</th>
<th>p</th>
<th>q</th>
<th>¹³C coupling constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>a±(b+c)/2</td>
</tr>
<tr>
<td>CCCCCCH</td>
<td>2395.12660(14)</td>
<td>127.48(3)</td>
<td>4.2762(16)</td>
<td>...</td>
<td>94.43(7)</td>
</tr>
<tr>
<td>¹³CCCH</td>
<td>2319.3514(1)</td>
<td>115(5)</td>
<td>4.1642(6)</td>
<td>...</td>
<td>24.40(8)</td>
</tr>
<tr>
<td>C¹³CCCCH</td>
<td>2375.3194(2)</td>
<td>127(5)</td>
<td>4.2648(7)</td>
<td>...</td>
<td>57.02(6)</td>
</tr>
<tr>
<td>C¹³CCCH</td>
<td>2394.9716(2)</td>
<td>135(6)</td>
<td>4.2484(7)</td>
<td>...</td>
<td>16.51(7)</td>
</tr>
<tr>
<td>C⁻¹³CH</td>
<td>2377.4127(2)</td>
<td>128(5)</td>
<td>4.2542(7)</td>
<td>...</td>
<td>29.55(8)</td>
</tr>
<tr>
<td>C⁻¹³CH</td>
<td>2327.8568(2)</td>
<td>121(5)</td>
<td>4.1823(7)</td>
<td>...</td>
<td>29.55(8)</td>
</tr>
</tbody>
</table>
| CCCCCCD          | 2262.12864(10) | 110.83(7) | 0.048(11) | −0.3244(20) | ... | ... | ...

Note: Units are in megahertz; uncertainties in parentheses are 1σ. Spectroscopic constants derived from data in EPAPS (Ref. 26).

The bonds have been determined to an accuracy of order 0.001 Å (Fig. 1), while the central bonds are less well determined to ~0.004 Å because the rotational constant of a linear chain is fairly insensitive to isotopic substitution near the center of mass. The bond lengths are compared in Table VI with equilibrium rₑ structures calculated ab initio at the RCCSD(T) level of theory^15 for each chain.

As in previous structural determinations, for the experimental (r₀) structures here no correction was made for zero point vibration. We have treated the rotation-vibration terms as a source of unknown error, which was estimated by assigning to each rotational constant an uncertainty which yields a reasonable value for χ² (a value of 2.3 was assigned, the most probable χ² for two degrees of freedom at a confidence interval of 1σ, Ref. 28). The uncertainty in B was assumed to be the same for each isotopic species included in the fit. The values so derived were ΔB=0.012 MHz for C₃H, ΔB=0.004 MHz for C₄H, and ΔB=0.001 MHz for C₅H.

The r₀ structures are generally in good agreement with the rₑ structures in Table VI. The theoretical and experimen-

Table VI. Experimental and theoretical bond lengths for C₃H, C₄H, and C₅H.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>C₃H</th>
<th>C₄H</th>
<th>C₅H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>Theory</td>
<td>Experiment</td>
</tr>
<tr>
<td>r(HC₁₀)</td>
<td>1.055(1)</td>
<td>1.065</td>
<td>1.056(1)</td>
</tr>
<tr>
<td>r(C₁₀C₁₁)</td>
<td>1.224(2)</td>
<td>1.228</td>
<td>1.216(2)</td>
</tr>
<tr>
<td>r(C₁₀C₁₁)</td>
<td>1.329(4)</td>
<td>1.339</td>
<td>1.341(4)</td>
</tr>
<tr>
<td>r(C₁₀C₁₁)</td>
<td>1.267(4)</td>
<td>1.273</td>
<td>1.237(5)</td>
</tr>
<tr>
<td>r(C₁₀C₁₁)</td>
<td>1.308(2)</td>
<td>1.318</td>
<td>1.332(4)</td>
</tr>
<tr>
<td>r(C₁₀C₁₁)</td>
<td>...</td>
<td>...</td>
<td>1.257(2)</td>
</tr>
<tr>
<td>r(C₁₀C₁₁)</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

^1Derived from a least-squares fit of the rotational constants of the isotopic species in Table V. Uncertainties (1σ) are in the last significant digit.

^2From Ref. 19. The C₃H and C₄H bond lengths were calculated at the RCCSD(T)/cc-pVQZ level of theory; those of C₅H were calculated at the RCCSD(T)/cc-pVDZ level of theory.
tional bond lengths for C₄H differ by no more than 0.010 Å, and, with the exception of the terminal C–C bond r(C(5)C(6)), those for C₆H differ by no more than 0.013 Å. For C₄H, the rₙ bonds are uniformly longer than those for the r₀ structure by ~0.03 Å, a difference probably attributable to the smaller basis set (cc-pVDZ) employed for this molecule. For C₆H and C₈H, each bond contracts by ~0.03 Å when a larger basis set (cc-pVTZ) is employed. If all the theoretical bond lengths of C₄H are decreased by this amount, the largest difference between two sets is reduced to only 0.012 Å. The r₀ structure of C₆H is also in agreement with the CCSD/TZP calculation of Crawford et al.,²⁹ in which the two sets of bonds differ by no more than 0.020 Å. The C–C bonds alternate in length along each chain, with the difference between successive bond lengths becoming more pronounced towards the hydrogen end. The bonding is probably best characterized as acetylenic in nature, but even this is very approximate, because many of the bonds are intermediate in length between standard triple and double bonds or double and single bonds.

V. DISCUSSION

The ¹³C hyperfine coupling constants of the odd-numbered radicals studied here exhibit a clear alternation in magnitude and sign along the heavy atom backbone. These constants are remarkably similar at each carbon atom regardless of chain length (see Fig. 4), and are largest at the terminal carbon. They decrease slowly in magnitude at alternate carbons on increase in distance from the terminal carbon. At the central carbon atom of C₃H, C₄H, and C₅H, and at the other alternating sets of carbon atoms of C₆H and C₇H, the hyperfine constants are of opposite sign compared to adjacent carbon positions, and are generally small in magnitude. These results suggest that the chemical bonding is very similar in the C₂n+H radicals, irrespective of chain length, and that the electron spin density is localized mainly on specific atoms; it is nearly zero at the carbon atom adjacent to the terminal carbon in each chain, and at alternate carbons down the chain as well. Recent theoretical calculations, performed at the B3LYP/cc-pVTZ (Ref. 30) level of theory, predict spin densities for each radical in good agreement—both in the magnitude and sign—with those measured here.

The ¹³C hyperfine constants are consistent with the classical picture of acetylenic rather than cumulenic structures for C₄H and C₆H, a conclusion which is supported by the structural determinations in Sec. IV. In C₆H, it is more difficult to determine the location of the unpaired electron because only a combination of terms [the diagonal term, a + (b + c)/2] and the off-diagonal term b are determinable from the present data. However the electron spin density is largest at the terminal carbon atom in this radical, and falls off slowly as the distance from the terminal carbon increases, implying a greater contribution from acetylenic bonding.

The present observations provide compelling evidence that spin polarization makes an important contribution not only to the Fermi-contact term bₑ, but to the hyperfine terms a, c, and d as well. A simple explanation for this effect has been pointed out by Brown⁵¹ and Kanada et al.,¹⁴ for C₄H, but it can be readily extended to longer chains. In the first-order molecular orbital description of C₆H, the unpaired electron occupies a nonbonding σ₂ orbital (where the axis x is perpendicular to the molecular axis z) which has a node at the central carbon atom, i.e., Cβ using the notation CₐC₈C₆H.¹⁴ Because the electron density is formally zero at this atom, there should be no hyperfine splitting. Owing to the well-established mechanism of spin polarization, however, bₑ is positive at the Cₐ and C₉ atoms and negative at the C₈ atom, because polarization of the paired electrons in the sigma bonds of this radical results in a net positive spin density at Cₐ and C₉ and a negative spin density at C₈, i.e., the atomic spin wave function is σ = -0.5 at this atom. Because the (negative) spin density is induced in the pₓ atomic orbital of Cβ, which possesses angular expectation values of
\[ \langle 3 \cos^2 \theta - 1 \rangle = -2/5 \text{ and } \langle \sin^2 \theta \rangle = 4/5, \]
the hyperfine parameter \( c \) will be positive and \( d \) will be negative. To retain the overall value for \( \Omega \) of the molecular wave function, the electronic quantum number \( \lambda \) at this atom must also be negative (i.e., the orbital angular momentum is also polarized); this effect arises via spin-orbit coupling which is comparably large. As a consequence, the hyperfine parameter \( a \) may also be negative. Because spin polarization is a second-order effect, all of the hyperfine parameters \( a, b_f, c, \) and \( d \) are generally small in magnitude.

The isotopic spectra of other long-chain radicals terminated with either oxygen or sulfur are probably accessible with the present technique. Lines of HC\(_2\)O chains as large as HC\(_2\)O and those of HC\(_3\)S up to HC\(_5\)S are sufficiently strong in our FTM spectrometer that their \(^{13}\)C isotopic species should be detectible in natural abundance with modest levels of integration. Isotopic studies of HC\(_3\)O radicals are worth doing because their structures are of theoretical interest\(^{32}\) and because these radicals are important in oxygen-hydrocarbon flames.\(^{33}\)

Astronomical searches for the isotopic species of C\(_2\)H, C\(_3\)H, and C\(_4\)H can now be conducted with high confidence using the molecular constants in Tables IV and V. The best place to look is probably IRC +10216, where the strongest lines of the normal isotopic species have already been found in the 2–3 mm band. Although the transitions in the upper fine-structure ladder have not been measured here, and the spin-orbit constant \( A_{so} \) may therefore be slightly different for each isotopic species, in IRC +10216 the width of rotational lines is very broad, of order 30 km s\(^{-1}\) in equivalent radial velocity—well in excess of the uncertainty from either the formal error of the molecular constants in Tables IV and V (0.6 km s\(^{-1}\)) or the estimated error in \( A_{so} \) upon isotopic substitution (~1% or about 3 km s\(^{-1}\)) at 100 GHz.

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25. There is apparently a systematic typographical error in Tables 1–3 of Ref. 14 which gives the millimeter-wave transition frequencies for each \(^{13}\)C isotopic species of C\(_2\)H. In each table, the \( \Omega \) labels should be reversed; those listed as originating from the \( \Omega=1/2 \) ladder are in fact from the \( \Omega=3/2 \) ladder, and vice versa.
26. See EPAPS Document No. E-JCP-SAS-122-017513 for complete lists of experimental transition frequencies. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached via the EPAPS homepage ([http://www.aip.org/pubservs/epaps.html](http://www.aip.org/pubservs/epaps.html)) or from ftp.aip.org in the directory /epaps. See the EPAPS homepage for more information.
30. S. Thorwirth (private communication).
31. J. M. Brown (private communication).