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# Experimental Structures of the Carbon Chains $HC_7N$, $HC_9N$, and $HC_{11}N$ by Isotopic Substitution

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The effective structures ($r_0$) of the three linear cyanopolyynes $HC_7N$, $HC_9N$, and $HC_{11}N$ have been determined to high accuracy by isotopic substitution, following detection in a supersonic molecular beam with a Fourier transform microwave spectrometer of all of the singly substituted rare isotopic species. For each chain, the lengths of the individual bonds have been determined to an accuracy of 0.001 Å or 0.1% toward the end of the chain and to 0.01 Å or 1.0% toward the center. The experimental structures are in excellent agreement with recent high-level theoretical calculations, or, in the case of $HC_{11}N$, with extrapolation from $HC_9N$. The three polyynes studied here represent the largest reactive carbon chain molecules for which accurate structures have been derived empirically. For $HC_7N$ and $HC_9N$, it has been possible to resolve at high-resolution nitrogen hyperfine structure in the lower rotational transitions and determine $eQq$ for all of the singly substituted isotopic species of $HC_7N$ and for normal $HC_9N$. © 2000 Academic Press

## INTRODUCTION

Linear carbon chains as large as $HC_{17}N$ have recently been detected in this laboratory in a supersonic molecular beam by Fourier transform microwave (FTM) spectroscopy (*1*). The refinements in instrumental sensitivity and production technique required to detect the longer chains now permit shorter ones to be observed with very high signal-to-noise, such that all the isotopic species with a single carbon-13 or nitrogen-15 are readily detected in natural abundance or with slight isotopic enrichment. Because rotational spectra can be rapidly acquired with our computer-controlled spectrometer, it is possible by isotopic substitution to determine precise effective ($r_0$) structures for fairly long chains within a homologous series to study how chemical bonding and electronic structure vary as a function of chain length. We do that here for the three cyanopolyynes $HC_7N$, $HC_9N$, and $HC_{11}N$. For the first two, *ab initio* values of the individual bond lengths have been calculated by Botschwina and co-workers (*2*, *3*), allowing a direct comparison of experiment with theory. The structures of $HC_3N$ (*4*) and $HC_5N$ (*5*) were determined by isotopic substitution some time ago, so with the work here a detailed comparison of the bonding in five successive cyanopolyynes is now in hand (Fig. 1).

## EXPERIMENTAL

A description of our FTM spectrometer and the discharge source used to produce the cyanopolyynes and other carbon chains is given elsewhere (*6*). Briefly, a pulsed supersonic molecular beam of an organic precursor vapor heavily diluted in an inert gas is produced by a commercial solenoid valve. Reactive molecules of many kinds are made by a small electrical discharge in the throat of the supersonic nozzle, prior to expansion of the gas into the large Fabry–Perot cavity of the spectrometer. The optimal production conditions for the present chains are similar to those for other closed-shell polyynes (*7*): a 1500–1800 V low-current gas discharge synchronized with a 200-$\mu$s-long gas pulse, with the best yields of $HC_9N$ and $HC_{11}N$ at the higher discharge voltages. At a stagnation pressure behind the pulsed valve of the nozzle of about 3 atm, flows are 15–20 sccm at a pulse rate of 6 Hz.

The lines of the single $^{13}C$ species of all three cyanopolyynes were readily observed without isotopic enrichment, using for a precursor gas a mixture of diacetylene and cyanoacetylene (0.5% each) heavily diluted in Ne, the blend which gives the strongest lines of the normal species. An increase in line intensity by a factor of 2 or more was easily achieved when a small amount (0.12%) of $^{13}C$-acetylene was added to the mixture; for speed and convenience, most of the $^{13}C$ measurements were made with this enrichment. Lines of $HC_7{}^{15}N$ and $HC_9{}^{15}N$, only marginally observed in natural abundance, were enhanced tenfold in intensity using a mixture of diacetylene (0.5%) and nitrogen (0.25%) enriched to over 99.9% in $^{15}N$, again diluted in Ne, a precursor combination found to produce strong lines of $HC_{11}{}^{15}N$ (*8*). For the three deuterated species, fully deuterated diacetylene was used in the diacetylene–cyanoacetylene mixture.

Good predictions for the rotational constants of the isotopic species studied here were made by scaling rotational constants calculated from the theoretical structures of $HC_7N$ (*2*) and $HC_9N$ (*3*), and from a structure of $HC_{11}N$ extrapolated from

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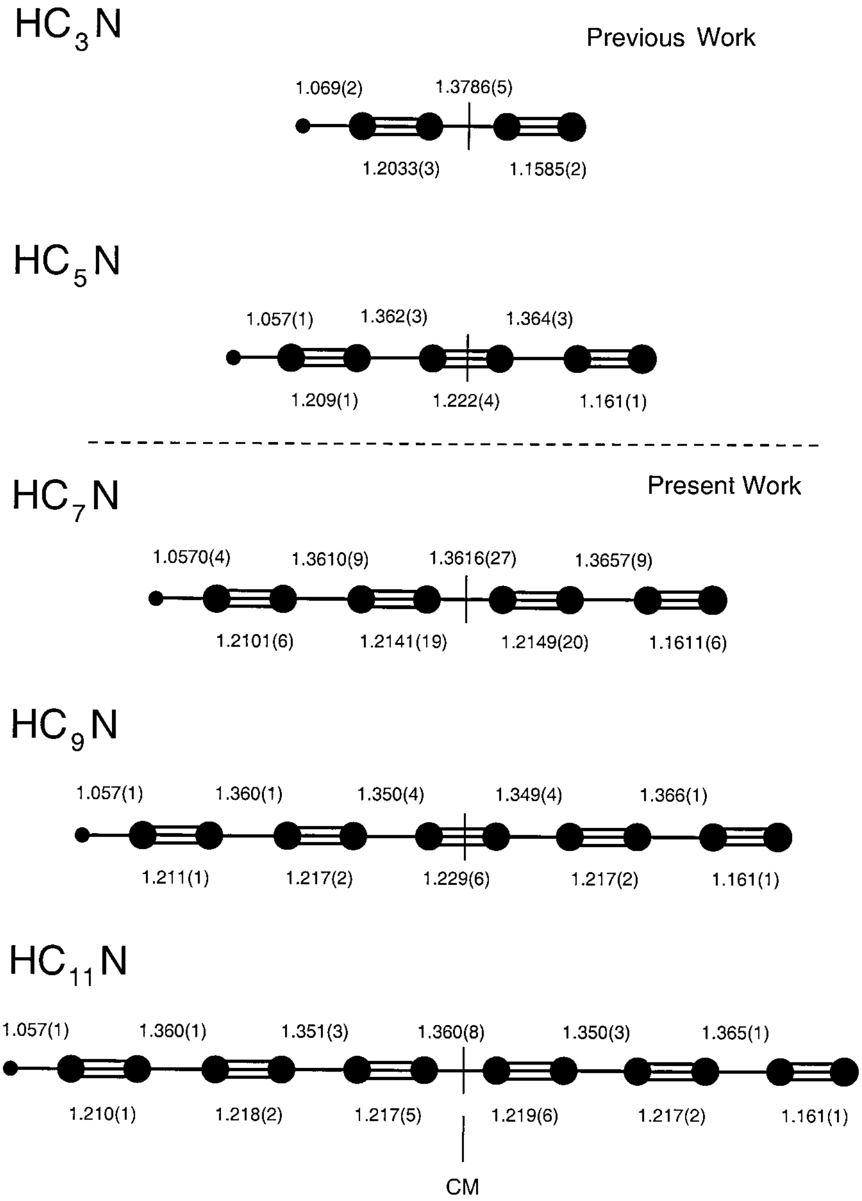


**FIG. 1.** Effective ($r_0$) structures of the cyanopolyynes (in Å) obtained by isotopic substitution. Uncertainties ($1\sigma$) are in the units of the last significant digit.

$HC_9N$ (see footnote to Table 7), by the ratio of the observed to the predicted rotational constant for the normal isotopic species of each cyanopolyyne. For all the singly substituted $^{13}C$ and $^{15}N$ isotopic lines, measured line frequencies typically agree with those predicted to within a few hundred kilohertz, so an extensive frequency search was not required. Owing to the large zero-point energies of the bending vibrations of the hydrogen atom, frequencies for the *D* species were less well predicted by scaling the theoretical geometries, but they were still good to about 1 MHz, allowing rapid and unambiguous detection of most of the lines of this species as well.

Under favorable conditions, hyperfine-split lines of the $^{13}C$ species of $HC_7N$ were observed with a signal-to-noise of nearly 40 in 5 min of integration, while a longer time, about 15 min, was required to observe the same lines of $HC_9N$ at comparable signal-to-noise (Fig. 2). For $HC_{11}N$, integration times of about 20 min were required to observe the lines of the 11 different $^{13}C$ species with a signal-to-noise of five, which with isotopic enrichment was increased to 10–15. It is interesting to note that with enrichment the line intensities of the singly substituted $^{13}C$ species are nearly equal for a given chain, indicating that in our discharge the carbon from the acetylene is randomly shuffled in the assembly of long chains.

## SPECTROSCOPIC ANALYSIS

Enough rotational transitions of each isotopic species were measured to determine precisely the rotational constant *B* and

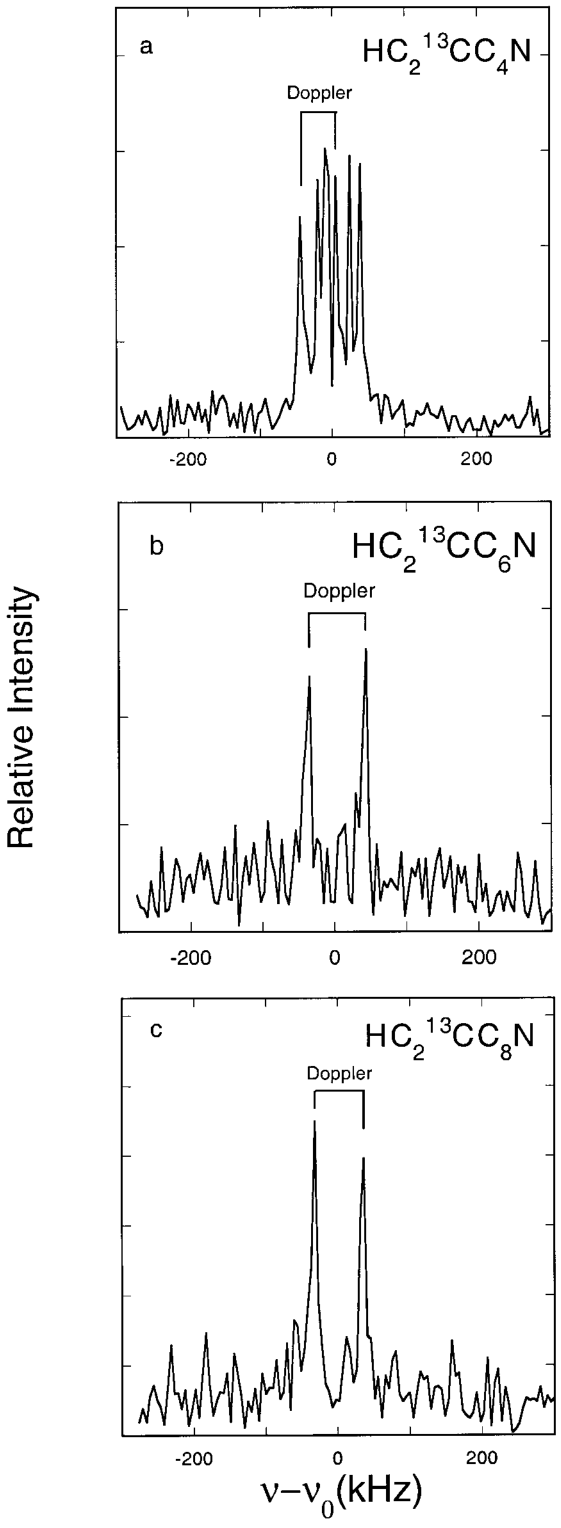


**FIG. 2.** Sample spectra of one of the $^{13}C$ isotopic species of each of the three cyanopolyynes. (a) The 7 → 6 transition of $HC_2{}^{13}CC_4N$ after 6 min of integration, showing nitrogen-quadrupole hyperfine structure and the characteristic double-peaked lineshape that results from the Doppler splitting due to the supersonic expansion of the molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry–Perot. (b) The 20 → 19 transition of $HC_2{}^{13}CC_6N$ after 3 min of integration. (c) The 29 → 28 transition of $HC_2{}^{13}CC_8N$ after 10 min of integration.

### TABLE 1
### Rotational Transitions of Normal $HC_7N$

| $J' \to J$ | $F' \to F$ | Frequency (MHz) |
|---|---|---|
| 6 → 5 | 5 → 4 | 6767.978 |
| | 6 → 5 | 6768.010 |
| | 7 → 6 | 6768.026 |
| 7 → 6 | 6 → 5 | 7895.989 |
| | 7 → 6 | 7896.010 |
| | 8 → 7 | 7896.023 |
| 8 → 7 | 7 → 6 | 9023.994 |
| | 8 → 7 | 9024.009 |
| | 9 → 8 | 9024.020 |
| 9 → 8 | 8 → 7 | 10151.996 |
| | 9 → 8 | 10152.007 |
| | 10 → 9 | 10152.017 |
| 10 → 9 | 9 → 8 | 11279.996 |
| | 10 → 9 | 11280.005 |
| | 11 → 10 | 11280.014 |
| 11 → 10 | 10 → 9 | 12407.994 |
| | 11 → 10 | 12408.002 |
| | 12 → 11 | 12408.010 |
| 12 → 11 | 11 → 10 | 13535.991 |
| | 12 → 11 | 13535.999 |
| | 13 → 12 | 13536.005 |
| 13 → 12 | 12 → 11 | 14663.987 |
| | 13 → 12 | 14663.993 |
| | 14 → 13 | 14663.999 |
| 14 → 13 | 13 → 12 | 15791.982 |
| | 14 → 13 | 15791.987 |
| | 15 → 14 | 15791.992 |
| 15 → 14 | 14 → 13 | 16919.974 |
| | 15 → 14 | 16919.980 |
| | 16 → 15 | 16919.983 |

NOTE. — Estimated experimental uncertainties (1σ) are 2 kHz. Observed minus calculated frequencies are 0-2 kHz; the best fit constants are given in Table 6.

the centrifugal distortion constant *D* of the three cyanopolyynes by fitting to the data the standard expression for the rotational transitions of a linear molecule, $\nu_{J\to J-1} = 2BJ - 4DJ^3$, where *J* is the angular momentum quantum number for the upper rotational level, and hfs from the nitrogen nucleus has been neglected. For $HC_7N$ and $HC_9N$, where nitrogen quadrupole hfs was resolved in the lower *J* transitions, a standard Hamiltonian which included hfs was used for the analysis. For the 36 isotopic species detected here, the rms of each fit is comparable to the measurement uncertainties of 1–3 kHz. Ten transitions were remeasured for normal $HC_7N$ (Table 1), and 18 for normal $HC_9N$ (Table 2). In all, seven transitions of nine rare isotopic species were measured for $HC_7N$ (Table 3), 10 transitions of 11 species of $HC_9N$ (Table 4), and 8 transitions of 13 species of $HC_{11}N$ (Table 5). All of the measured lines lie between 6 and 17 GHz, the frequency band where the rotational transitions of the present molecules are most intense in our cold molecular beam ($T_{rot} \sim 2.5$ K). The best-fit spectroscopic constants are given in Table 6.

For normal $HC_7N$ and $HC_9N$, the rotational and centrifugal distortion constants agree to within the measurement uncer-

### TABLE 2
### Rotational Transitions of Normal $HC_9N$

| $J' \to J$ | $F' \to F$ | Frequency (MHz) |
|---|---|---|
| 10 → 9 | 9 → 8 | 5810.352 |
| | 10 → 9 | 5810.362 |
| | 11 → 10 | 5810.370 |
| 11 → 10 | 10 → 9 | 6391.390 |
| | 11 → 10 | 6391.398 |
| | 12 → 11 | 6391.404 |
| 12 → 11 | 11 → 10 | 6972.426 |
| | 12 → 11 | 6972.434 |
| | 13 → 12 | 6972.440 |
| 13 → 12 | 12 → 11 | 7553.462 |
| | 13 → 12 | 7553.469 |
| | 14 → 13 | 7553.474 |
| 14 → 13 | 13 → 12 | 8134.498 |
| | 14 → 13 | 8134.503 |
| | 15 → 14 | 8134.508 |
| 15 → 14 | 14 → 13 | 8715.533 |
| | 15 → 14 | 8715.538 |
| | 16 → 15 | 8715.542 |
| 18 → 17 | | 10458.638 |
| 19 → 18 | | 11039.673 |
| 20 → 19 | | 11620.706 |
| 21 → 20 | | 12201.738 |
| 22 → 21 | | 12782.770 |
| 23 → 22 | | 13363.800 |
| 24 → 23 | | 13944.831 |
| 25 → 24 | | 14525.862 |
| 26 → 25 | | 15106.891 |
| 27 → 26 | | 15687.921 |
| 28 → 27 | | 16268.950 |
| 29 → 28 | | 16849.980 |

*Note.* Estimated experimental uncertainties ($1\sigma$) are 2 kHz. Observed minus calculated frequencies and best fit constants as in Table 1.

tainties with previously published values: $B = 564.00074 \pm 0.00016$ MHz and $D = 3.821 \pm 0.087$ Hz for $HC_7N$ by Kirby *et al.* (*9*), and $B = 290.518322 \pm 0.000057$ MHz and $D = 0.874 \pm 0.078$ Hz for $HC_9N$ by Iida *et al.* (*10*). Owing to the strong lines here and the use of an axially oriented molecular beam yielding extremely sharp lines (a FWHM typically of 5 kHz), our constants for these two chains are more than three times as accurate as those previously published. As Table 6 shows, the quadrupole coupling constants for both are in good agreement with those found for $HC_3N$ and $HC_5N$.

Line misidentifications will quickly poison structural determinations made by isotopic substitution, so considerable care was taken to avoid them. To assure that each of the many lines analyzed was part of a smooth harmonic progression and that none of the nearly 400 isotopic lines in Tables 3–5 was misassigned, many more lines in each rotational ladder were measured than strictly speaking are required to determine $B$ and $D$. By deviating from the expected harmonic progression in each ladder, misidentified lines were quickly spotted and eliminated from the data set (very few were in fact encountered). Line intensities in a given ladder were shown to be close to those expected and were shown as well to increase as expected on isotopic enrichment. As required for closed-shell molecules such as the cyanopolyynes, the assigned lines exhibit no appreciable Zeeman effect when a large permanent magnet is brought near the molecular beam. As a final demonstration of consistency in support of the assignments, we note that the centrifugal distortion constants of the isotopic

### TABLE 3
### Rotational Transitions of the Singly Substituted Isotopic Species of $HC_7N$ (in MHz)

| $J' \to J$ | $F' \to F$ | $DC_7N$ | $H^{13}CC_6N$ | $HC^{13}CC_5N$ | $HC_2{}^{13}CC_4N$ | $HC_3{}^{13}CC_3N$ | $HC_4{}^{13}CC_2N$ | $HC_5{}^{13}CCN$ | $HC_6{}^{13}CN$ | $HC_7{}^{15}N$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 7 → 6 | 6 → 5 | 7634.386 | 7722.989 | 7802.622 | 7863.681 | 7891.532 | 7892.225 | 7865.553 | 7805.524 | |
| | 7 → 6 | 7634.407 | 7723.011 | 7802.644 | 7863.703 | 7891.554 | 7892.247 | 7865.574 | 7805.547 | 7731.542 |
| | 8 → 7 | 7634.421 | 7723.023 | 7802.658 | 7863.716 | 7891.567 | 7892.260 | 7865.588 | 7805.559 | |
| 8 → 7 | 7 → 6 | 8725.020 | 8826.279 | 8917.290 | 8987.072 | 9018.900 | 9019.693 | 8989.209 | 8920.606 | |
| | 8 → 7 | 8725.035 | 8826.295 | 8917.306 | 8987.088 | 9018.916 | 9019.708 | 8989.225 | 8920.622 | 8836.046 |
| | 9 → 8 | 8725.046 | 8826.306 | 8917.316 | 8987.098 | 9018.928 | 9019.720 | 8989.236 | 8920.632 | |
| 9 → 8 | 8 → 7 | 9815.650 | 9929.568 | 10031.955 | 10110.458 | 10146.266 | 10147.158 | 10112.864 | 10035.686 | |
| | 9 → 8 | 9815.662 | 9929.580 | 10031.967 | 10110.470 | 10146.278 | 10147.169 | 10112.875 | 10035.696 | 9940.549 |
| | 10 → 9 | 9815.672 | 9929.588 | 10031.976 | 10110.479 | 10146.288 | 10147.179 | 10112.886 | 10035.706 | |
| 10 → 9 | 9 → 8 | 10906.280 | 11032.853 | 11146.623 | 11233.843 | 11273.629 | 11274.618 | 11236.517 | 11150.762 | |
| | 10 → 9 | 10906.288 | 11032.863 | 11146.632 | 11233.853 | 11273.638 | 11274.629 | 11236.526 | 11150.771 | 11045.052 |
| | 11 → 10 | 10906.296 | 11032.873 | 11146.638 | 11233.863 | 11273.648 | 11274.639 | 11236.534 | 11150.779 | |
| 11 → 10 | 10 → 9 | 11996.906 | 12136.137 | 12261.276 | 12357.224 | 12400.991 | 12402.084 | 12360.165 | 12265.835 | |
| | 11 → 10 | 11996.914 | 12136.146 | 12261.286 | 12357.236 | 12401.000 | 12402.093 | 12360.175 | 12265.845 | 12149.553 |
| | 12 → 11 | 11996.921 | 12136.153 | 12261.292 | 12357.242 | 12401.007 | 12402.100 | 12360.182 | 12265.852 | |
| 12 → 11 | 11 → 10 | 13087.532 | 13239.419 | 13375.936 | 13480.607 | 13528.350 | 13529.540 | 13483.816 | 13380.911 | |
| | 12 → 11 | 13087.538 | 13239.427 | 13375.947 | 13480.615 | 13528.359 | 13529.548 | 13483.824 | 13380.917 | 13254.054 |
| | 13 → 12 | 13087.545 | 13239.434 | 13375.952 | 13480.621 | 13528.366 | 13529.554 | 13483.830 | 13380.925 | |
| 13 → 12 | 12 → 11 | 14178.156 | 14342.703 | 14490.594 | 14603.988 | 14655.712 | 14656.998 | 14607.463 | 14495.983 | |
| | 13 → 12 | 14178.161 | 14342.709 | 14490.601 | 14603.996 | 14655.718 | 14657.006 | 14607.470 | 14495.990 | 14358.553 |
| | 14 → 13 | 14178.168 | 14342.714 | 14490.606 | 14604.000 | 14655.723 | 14657.010 | 14607.476 | 14495.995 | |

NOTE. — Estimated experimental uncertainties ($1\sigma$) are 2 kHz. Observed minus calculated frequencies and the best fit constants as in Table 1.

**TABLE 4**

**Rotational Transitions of the Singly Substituted Isotopic Species of $HC_9N$ (in MHz)**

| $J' \rightarrow J$ | $DC_9N$ | $H^{13}CC_8N$ | $HC^{13}CC_7N$ | $HC_2{}^{13}CC_6N$ | $HC_3{}^{13}CC_5N$ | $HC_4{}^{13}CC_4N$ | $HC_5{}^{13}CC_3N$ | $HC_6{}^{13}CC_2N$ | $HC_7{}^{13}CCN$ | $HC_8{}^{13}CN$ | $HC_9{}^{15}N$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14 → 13 | 7921.710[a] | 7981.644 | 8038.231 | 8086.654 | 8115.936 | 8132.518 | 8132.872 | 8117.147 | 8088.624 | 8040.777 | 7988.246 |
| 15 → 14 | 8487.544[a] | 8551.760 | 8612.386 | 8664.271 | 8695.648 | 8713.412 | 8713.793 | 8696.937 | 8666.379 | 8615.113 | 8558.833 |
| 16 → 15 | 9053.381[a] | 9121.878 | 9186.542 | 9241.888 | 9275.354 | 9294.300 | 9294.710 | 9276.735 | 9244.138 | 9189.456 | 9129.420 |
| 17 → 16 | 9619.215[a] | 9691.992 | 9760.700 | 9819.505 | 9855.060 | 9875.195 | 9875.630 | 9856.528 | 9821.893 | 9763.792 | 9700.008 |
| 18 → 17 | 10185.047 | 10262.106 | 10334.857 | 10397.121 | 10434.772 | 10456.084 | 10456.547 | 10436.323 | 10399.649 | 10338.130 | 10270.594 |
| 19 → 18 | 10750.884 | 10832.225 | 10909.013 | 10974.736 | 11014.478 | 11036.975 | 11037.461 | 11016.112 | 10977.402 | 10912.471 | 10841.180 |
| 20 → 19 | 11316.715 | 11402.339 | 11483.167 | 11552.351 | 11594.184 | 11617.869 | 11618.379 | 11595.907 | 11555.158 | 11486.809 | 11411.766 |
| 21 → 20 | 11882.548 | 11972.451 | 12057.321 | 12129.964 | 12173.889 | 12198.757 | 12199.292 | 12175.698 | 12132.912 | 12061.146 | 11982.352 |
| 22 → 21 | 12448.381 | 12542.562 | 12631.478 | 12707.578 | 12753.594 | 12779.642 | 12780.208 | 12755.488 | 12710.669 | 12635.482 | 12552.937 |
| 23 → 22 | 13014.214 | 13112.676 | 13205.630 | 13285.191 | 13333.300 | 13360.538 | 13361.123 | …… | 13288.421 | 13209.816 | 13123.522 |

NOTE. — Estimated experimental uncertainties (1σ) are 2 kHz. Observed minus calculated frequencies and the best fit constants as in Table 1.

[a] Center of hyperfine-split transition.

species of a given chain, as required, are all very nearly the same (Table 6).

Although we can therefore be highly confident that there are no misassignments of lines to rotational ladders in Tables 3–5, it is important to be certain as well that the ladders are correctly assigned to the various isotopic species. As Fig. 1 shows, the center of mass (CM) of the cyanopolyynes falls very close to the central bond of the heavy atom backbone of the molecule. As a result, as Fig. 3 shows, all but one of the carbon-13 shifts occur in tightly spaced pairs, corresponding to the two carbon atoms at about the same distance from the CM. For the inner carbon pairs especially, the splitting in $B$ is comparable to the uncertainty in the *a priori* isotope shifts in $B$. How then can one determine which rotational ladder corresponds to which carbon atom? Fortunately, this ambiguity is easily resolved, because for all reasonable *a priori* structures, even ones with cumulenic double bonds, the CM is displaced from the midpoint of the central carbon–carbon bond in the same direction: toward the terminal nitrogen atom. As a consequence, in each pair of rotational ladders in Table 6, the ladder with the higher $B$ can be assigned without ambiguity to the carbon atom in the corresponding pair which is closest to the nitrogen end of the chain.

## STRUCTURAL DETERMINATIONS

For each cyanopolyyne, effective ($r_0$) structures were determined from a least-squares fit of all the bonds in the molecule to the measured rotational constants in Table 6, 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 the bonds have been determined to remarkably high accuracy for molecules so large, of order 0.001 Å (Fig. 1). Equally remarkable, the derived bonds agree with those calculated *ab initio* to about the same accuracy (Table 7). Because the rotational constant of a linear chain is insensitive to isotopic substitution near the center of mass, the central bonds are not so accurately determined, but are still good to about 0.01 Å; these too are in very satisfactory agreement with theory, or in the case of $HC_{11}N$, with those predicted by extrapolation from $HC_9N$. Because substitution structures give even larger uncertainties for the central bond lengths, we have chosen not to report them here.

For the effective 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 $\chi^2$ [a value of 2.3 was assigned, the most probable $\chi^2$ for two degrees of freedom (*11*)]. The uncertainty in $B$ was assumed to be the same for each isotopic species included in a given fit. The values so derived were $\Delta B = 0.0030$ MHz for $HC_7N$, 0.0055 MHz for $HC_9N$, and 0.0085 MHz for $HC_{11}N$.

It might seem strange that rotational constants which can be fit to $10^{-5}$ yield bonds which at best are good to $10^{-3}$. The uncertainty in a given bond, however, is highly anticorrelated with that of each adjacent bond, and when this anticorrelation is taken into account in the propagation of errors by means of the covariance matrix of the fit, it is found that the best fit

**TABLE 5**

**Rotational Transitions of the Singly Substituted Isotopic Species of $HC_{11}N$ (in MHz)**

| $J' \rightarrow J$ | $DC_{11}N$ | $H^{13}CC_{10}N$ | $HC^{13}CC_9N$ | $HC_2{}^{13}CC_8N$ | $HC_3{}^{13}CC_7N$ | $HC_4{}^{13}CC_6N$ | $HC_5{}^{13}CC_5N$ | $HC_6{}^{13}CC_4N$ | $HC_7{}^{13}CC_3N$ | $HC_8{}^{13}CC_2N$ | $HC_9{}^{13}CCN$ | $HC_{10}{}^{13}CN$ | $HC_{11}{}^{15}N$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 26 → 25 | 8601.142 | 8646.992 | 8691.624 | 8732.187 | 8759.706 | 8780.268 | 8789.707 | 8789.998 | 8781.066 | …… | 8734.098 | 8693.905 | 8652.538 |
| 27 → 26 | 8931.958 | …… | 9025.914 | 9068.038 | 9096.610 | 9117.969 | 9127.766 | 9128.076 | 9118.793 | 9098.034 | 9070.020 | 9028.284 | 8985.325 |
| 28 → 27 | 9262.763 | 9312.146 | 9360.208 | 9403.893 | 9433.522 | 9455.668 | 9465.827 | 9466.152 | 9456.520 | 9434.997 | 9405.950 | …… | 9318.110 |
| 29 → 28 | 9593.576 | 9644.721 | 9694.502 | 9739.743 | 9770.432 | 9793.369 | 9803.896 | 9804.223 | 9794.255 | 9771.964 | 9741.872 | 9697.045 | 9650.900 |
| 30 → 29 | 9924.387 | 9977.291 | 10028.791 | 10075.591 | 10107.341 | 10131.067 | 10141.954 | 10142.302 | 10131.986 | 10108.923 | 10077.798 | 10031.421 | 9983.685 |
| 31 → 30 | 10255.200 | 10309.868 | 10363.082 | 10411.444 | 10444.254 | …… | 10480.018 | 10480.376 | …… | 10445.883 | 10413.724 | 10365.803 | 10316.475 |
| 32 → 31 | 10586.010 | 10642.442 | 10697.376 | 10747.296 | 10781.160 | 10806.473 | 10818.082 | 10818.452 | 10807.448 | 10782.846 | 10749.649 | 10700.183 | 10649.265 |
| 33 → 32 | 10916.820 | 10975.018 | 11031.666 | 11083.147 | 11118.071 | 11144.170 | 11156.148 | 11156.526 | 11145.180 | 11119.810 | 11085.571 | 11034.560 | 10982.051 |

NOTE. — Estimated experimental uncertainties (1σ) are 2 kHz. Observed minus calculated frequencies and the best fit constants as in Table 1.

bonds with the uncertainties given here reproduce the rotational constants to the claimed $10^{-5}$ or better, a useful consistency check on the numerical analysis.

## DISCUSSION

The present work provides the first empirical evidence that well-defined bond alternation, as predicted by theory, exists throughout a fairly long polyyne chain. There is no evidence in $HC_{11}N$, for example, of a tendency of the central bonds to even out, approaching those of a cumulenic, double-bonded structure, as observed for example in the shorter cumulenic chains $H_2CCC$ (*12*) and $H_2CCCC$ (*13*), and predicted for longer members of that series (*14*). Presumably, bond alternation persists in the limit of the infinite polyyne chain because it also persists in the polyenes, which are the somewhat similar stable carbon chains with alternating single and double bonds whose structures have been studied extensively by X-ray diffraction (*15*).

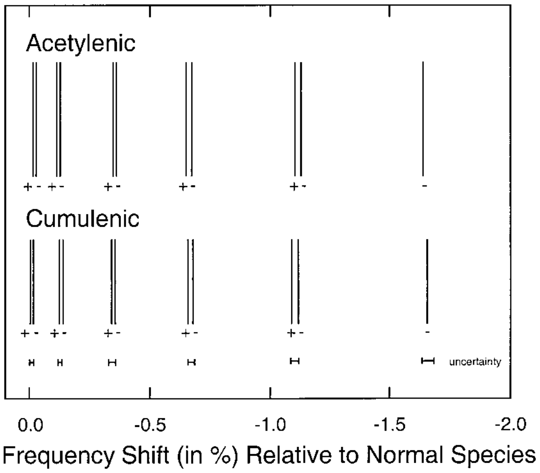


**FIG. 3.** Carbon-13 isotopic shifts of $HC_{11}N$ from two different *a priori* structures. The isotopic shifts occur in tightly spaced pairs for either acetylenic or cumulenic bonding since the center of mass is nearly midpoint between the central carbon–carbon bond, but is slightly displaced toward the terminal nitrogen atom. The plus (+) signs indicate $^{13}C$ shifts toward the nitrogen side of the center of mass. Uncertainties are approximately proportional to the magnitude of the frequency shifts.

**TABLE 6**

**Spectroscopic Constants of the Isotopic Species of $HC_7N$, $HC_9N$, and $HC_{11}N$ in (MHz)**

| Molecule | *B* | *D* x $10^6$ | *eqQ*[a] |
|---|---|---|---|
| $HC_7N$ | 564.00112(5) | 4.02(15) | -4.29(16) |
| $HC_4{}^{13}CC_2N$ | 563.73236(7) | 4.06(28) | -4.51(22) |
| $HC_3{}^{13}CC_3N$ | 563.68282(7) | 4.07(28) | -4.53(22) |
| $HC_5{}^{13}CCN$ | 561.82714(7) | 4.03(27) | -4.46(22) |
| $HC_2{}^{13}CC_4N$ | 561.69352(7) | 4.18(28) | -4.50(22) |
| $HC_6{}^{13}CN$ | 557.53939(7) | 3.95(28) | -4.37(22) |
| $HC^{13}CC_5N$ | 557.33224(7) | 4.16(28) | -4.45(22) |
| $HC_7{}^{15}N$ | 552.25338(12) | 3.96(48) | |
| $H^{13}CC_6N$ | 551.64401(7) | 4.06(28) | -4.41(22) |
| $DC_7N$ | 545.31523(7) | 3.85(28) | -4.33(22) |
| $HC_9N$ | 290.51832(1) | 0.860(10) | -4.84(21) |
| $HC_5{}^{13}CC_3N$ | 290.46018(6) | 0.924(81) | |
| $HC_4{}^{13}CC_4N$ | 290.44743(6) | 0.961(81) | |
| $HC_6{}^{13}CC_2N$ | 289.89853(8) | 1.090(110) | |
| $HC_3{}^{13}CC_5N$ | 289.85527(6) | 0.869(80) | |
| $HC_7{}^{13}CCN$ | 288.87979(6) | 1.020(80) | |
| $HC_2{}^{13}CC_6N$ | 288.80947(6) | 0.901(81) | |
| $HC_8{}^{13}CN$ | 287.17092(6) | 0.919(81) | |
| $HC^{13}CC_7N$ | 287.08002(6) | 1.040(80) | |
| $HC_9{}^{15}N$ | 285.29480(6) | 0.800(81) | |
| $H^{13}CC_8N$ | 285.05909(6) | 0.850(81) | |
| $DC_9N$ | 282.91852(6) | 0.787(74) | |
| $HC_{11}N$ | 169.06295(3)[b] | 0.242(14)[b] | |
| $HC_6{}^{13}CC_4N$ | 169.03871(8) | 0.201(44) | |
| $HC_5{}^{13}CC_5N$ | 169.03316(8) | 0.302(44) | |
| $HC_7{}^{13}CC_3N$ | 168.86694(8) | 0.277(45) | |
| $HC_4{}^{13}CC_6N$ | 168.85165(8) | 0.267(44) | |
| $HC_8{}^{13}CC_2N$ | 168.48249(10) | 0.246(53) | |
| $HC_3{}^{13}CC_7N$ | 168.45616(8) | 0.251(44) | |
| $HC_9{}^{13}CCN$ | 167.96371(8) | 0.228(44) | |
| $HC_2{}^{13}CC_8N$ | 167.92703(8) | 0.260(43) | |
| $HC_{10}{}^{13}CN$ | 167.19074(8) | 0.194(45) | |
| $HC^{13}CC_9N$ | 167.14684(8) | 0.176(44) | |
| $HC_{11}{}^{15}N$ | 166.39526(7) | 0.254(36) | |
| $H^{13}CC_{10}N$ | 166.28861(8) | 0.209(39) | |
| $DC_{11}N$ | 165.40694(7) | 0.265(36) | |

*Note.* Uncertainties (in parentheses) are in the last significant digit.

[a] $eQq = -4.319(1)$ MHz for $HC_3N$ (Ref. *16*) and $eQq = -4.242(30)$ MHz for $HC_5N$ (Ref. *17*).

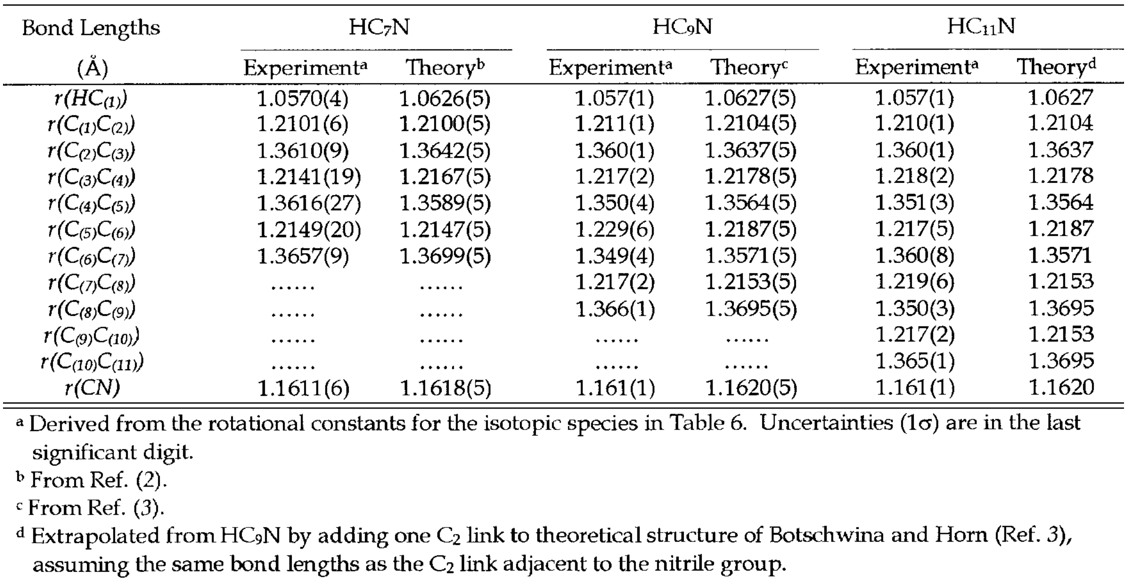
[b] From Ref. (*8*).

With instrumental improvements, it may be possible to extend the present techniques to somewhat longer polyynes, say to $HC_{13}N$ and $HC_{15}N$, but beyond that size reduced signal-to-noise and misidentification of lines are likely to make progress both tedious and error prone. Polyyne chains are highly unstable, even short ones like diacetylene tending to explosive polymerization, so X-ray diffraction, requiring dense samples, would not appear to be a viable method of structural determination.

It is interesting to note in Table 7 how well the empirical bonds here, derived by neglecting zero point vibration entirely, agree with the equilibrium bonds $r_e$ calculated *ab initio.* Zero-point vibration of the stretching modes will tend to increase the length of a linear chain and lower its rotational constant, while that of the bending modes in contrast will tend to decrease the length and raise the rotational constant. One wonders if at some chain length the cancellation is complete, and the $r_0$ and the $r_e$ structures are essentially identical.

Finally, we note that Table 6 provides all the data needed (the precise rest frequencies) for astronomical searches for the rare isotopic species of the present carbon chains, all three of which have been found in the normal isotopic species in at least one astronomical source. The best place to look is probably the cold, narrow-line molecular cloud TMC-1 in the Taurus dark clouds, where the width of rotational lines is typically 1 km $s^{-1}$ in equivalent radial velocity. The constants in Table 6 allow all the lower rotational transitions of the chains here, those of

**TABLE 7**
**Experimental and Theoretical Bond Lengths for $HC_7N$, $HC_9N$, and $HC_{11}N$**



| Bond Lengths | $HC_7N$ | | $HC_9N$ | | $HC_{11}N$ | |
|---|---|---|---|---|---|---|
| (Å) | Experiment[a] | Theory[b] | Experiment[a] | Theory[c] | Experiment[a] | Theory[d] |
| $r(HC_{(1)})$ | 1.0570(4) | 1.0626(5) | 1.057(1) | 1.0627(5) | 1.057(1) | 1.0627 |
| $r(C_{(1)}C_{(2)})$ | 1.2101(6) | 1.2100(5) | 1.211(1) | 1.2104(5) | 1.210(1) | 1.2104 |
| $r(C_{(2)}C_{(3)})$ | 1.3610(9) | 1.3642(5) | 1.360(1) | 1.3637(5) | 1.360(1) | 1.3637 |
| $r(C_{(3)}C_{(4)})$ | 1.2141(19) | 1.2167(5) | 1.217(2) | 1.2178(5) | 1.218(2) | 1.2178 |
| $r(C_{(4)}C_{(5)})$ | 1.3616(27) | 1.3589(5) | 1.350(4) | 1.3564(5) | 1.351(3) | 1.3564 |
| $r(C_{(5)}C_{(6)})$ | 1.2149(20) | 1.2147(5) | 1.229(6) | 1.2187(5) | 1.217(5) | 1.2187 |
| $r(C_{(6)}C_{(7)})$ | 1.3657(9) | 1.3699(5) | 1.349(4) | 1.3571(5) | 1.360(8) | 1.3571 |
| $r(C_{(7)}C_{(8)})$ | …… | …… | 1.217(2) | 1.2153(5) | 1.219(6) | 1.2153 |
| $r(C_{(8)}C_{(9)})$ | …… | …… | 1.366(1) | 1.3695(5) | 1.350(3) | 1.3695 |
| $r(C_{(9)}C_{(10)})$ | …… | …… | …… | …… | 1.217(2) | 1.2153 |
| $r(C_{(10)}C_{(11)})$ | …… | …… | …… | …… | 1.365(1) | 1.3695 |
| $r(CN)$ | 1.1611(6) | 1.1618(5) | 1.161(1) | 1.1620(5) | 1.161(1) | 1.1620 |

[a] Derived from the rotational constants for the isotopic species in Table 6. Uncertainties ($1\sigma$) are in the last significant digit.

[b] From Ref. (2).

[c] From Ref. (3).

[d] Extrapolated from $HC_9N$ by adding one $C_2$ link to theoretical structure of Botschwina and Horn (Ref. 3), assuming the same bond lengths as the $C_2$ link adjacent to the nitrile group.

major astronomical interest, to be calculated to 0.02–0.2 km $s^{-1}$, a small fraction of a linewidth.

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