JOURNAL OF CHEMICAL PHYSICS VOLUME 109, NUMBER 8 22 AUGUST 1998

The isocyanopolyynes HC_4NC and HC_6NC: Microwave spectra and *ab initio* calculations

P. Botschwina[a] and Ä. Heyl
Institut für Physikalische Chemie der Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany

W. Chen, M. C. McCarthy, J.-U. Grabow, M. J. Travers, and P. Thaddeus
Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138
and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

(Received 21 April 1998; accepted 22 May 1998)

Rotational spectra of HC_4NC and HC_6NC, linear molecules of interest to interstellar cloud chemistry, were recorded by Fourier transform microwave spectroscopy, and the ground state rotational constants were determined to be 1401.18227(7) and 582.5203(1) MHz. Nitrogen quadrupole hyperfine structure could be observed for HC_4NC. On the basis of coupled cluster calculations including connected triple substitutions accurate equilibrium structures (uncertainty in bond lengths ca. 0.0005 Å) could be established for both species. The equilibrium dipole moments, predicted to be -3.25 and -3.49 D for HC_4NC and HC_6NC, respectively, exhibit large correlation effects of 30% and 33%. © *1998 American Institute of Physics.* [S0021-9606(98)01032-0]

I. INTRODUCTION

While the cyanopolyynes ($HC_{2n+1}N$) are known interstellar molecules up to $n=5$[1] and have been spectroscopically investigated up to $n=8$,[2] rather little is known about the corresponding isocyanopolyynes ($HC_{2n}NC$). Only isocyanoacetylene (HC_2NC) has so far been studied by various spectroscopic techniques and by radioastronomy. Following an accurate prediction of its equilibrium rotational constant of $B_e=4964$ MHz by Botschwina and Sebald in 1983,[3] the first microwave spectrum of HC_2NC was reported in 1991 by Krüger *et al.*[4] and the ground-state rotational constant was determined to be $B_0=4967.8370(3)$ MHz. On the basis of the laboratory measurements, already available interstellar lines could be readily assigned to rotational transitions in HC_2NC.[5] The microwave and millimeter-wave work on HC_2NC isotopomers was considerably extended in later work,[6–8] and photoelectron spectra[9] and high-resolution infrared spectra[10] could be recorded.

The present paper is devoted to a joint experimental/theoretical study of the next members of the isocyanopolyyne series, HC_4NC and HC_6NC. The experimental work makes use of Fourier transform microwave (FTM) spectroscopy and was carried out at Harvard. It should provide valuable information for forthcoming investigations of the two species in the interstellar medium by means of radio astronomy. *Ab initio* calculations were carried out at Göttingen. The theoretical study on HC_4NC represents a considerable extension over our previous work on this species.[11] To the authors' knowledge, no high-quality *ab initio* calculations have yet been published for HC_6NC.

II. EXPERIMENT

The rotational spectra of the isocyanopolyynes HC_4NC and HC_6NC were detected in a supersonic molecular beam by FTM spectroscopy.[12] The conditions for optimal production of these carbon chains were nearly identical to those that yield the strongest lines of the cyanopolyynes:[2] a low-current dc discharge (1200 V) synchronized with a 210 μs long gas pulse at a total pressure behind the nozzle of 2 atm. Although a dilute gas sample of methylcyanoacetylene (CH_3CCCN) and diacetylene (HC_4H, 1% each) in Ne was used for most of the experiments, lines of HC_4NC and HC_6NC were also produced with nearly equal intensity with 1% cyanoacetylene (HC_3N) in Ne and two other mixtures: one of diacetylene and cyanogen (C_2N_2, 1% each) in Ne, the other of diacetylene and cyanoacetylene (1% each) in Ne.

The two new chains were detected with the same sensitive reactive molecule FTM spectrometer[13] recently used to detect the rotational transitions of $HC_{15}N$, $HC_{17}N$,[2] and a number of other long carbon chains and ring chains.[14] Since its construction two years ago, several improvements have been made to this spectrometer, which increases its detection sensitivity by about a factor of 5. These include increasing the duty cycle of the molecular beam source by improving the pumping speed of the system, better coupling between the Fabry–Perot and the first stage of amplifier of the receiver, and cooling the cavity mirrors of the Fabry–Perot and first-stage amplifier to 77 K.[15]

Under optimized experimental conditions, the intensities of the strongest lines of HC_4NC and HC_6NC are about 200 and 400 times weaker, respectively, than those of their more stable counterparts, the cyanopolyynes HC_5N and HC_7N. HC_4NC is approximately 20 times stronger than HC_6NC under those conditions, nearly the same decrement in line intensity as observed on ascending the cyanopolyyne series from HC_5N to HC_7N. Strong lines of HC_4NC were easily observed in a few minutes of integration, but proportionally longer integrations were required to achieve comparable signals for HC_6NC, e.g., about 20 min to achieve a signal to noise of 10–20. No attempt was made to detect the next

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[a] Electronic mail: pbotsch@gfwdg.de

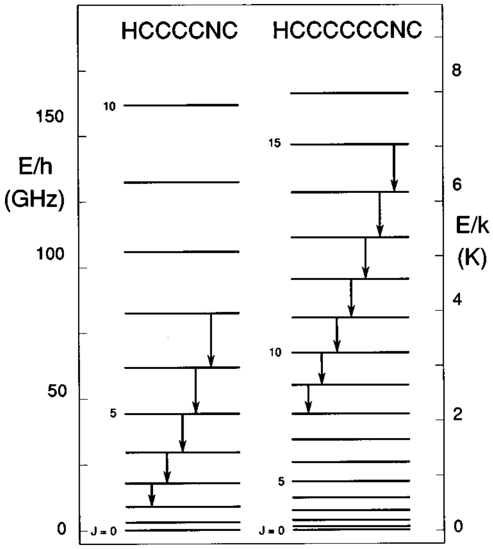

FIG. 1. Lower rotational levels of HC_4NC and HC_6NC. Arrows indicate the rotational transitions measured.

member in the series, HC_8NC, since currently many hours of integration would be required to observe its faint rotational lines if the same intensity decrement continues beyond HC_6NC. With modest improvements in production efficiency or sensitivity, however, this chain should be within reach. Little frequency search is probably required: the rotational constant predicted from theoretical calculations or estimated from extrapolations from the shorter members of the series is only uncertain to the order of ±0.01%.

III. DATA AND ANALYSIS

The observed rotational transitions are shown in Fig. 1, the measured laboratory frequencies between 8 and 20 GHz are given in Tables I and II, and typical lines are shown in Fig. 2. For both molecules, the rotational and leading centrifugal distortion constants were determined by fitting the

TABLE I. Measured rotational transitions of HC_4NC.

Frequency[a] (MHz)	O–C[b] (kHz)	$J'-J$	$F'-F$
8407.078	0	3–2	4–3
8407.090	0		3–2
8407.138	0		2–1
11 209.442	0	4–3	5–4
11 209.450	1		4–3
11 209.468	−2		3–2
14 011.800	0	5–4	6–5
14 011.806	0		5–4
14 011.819	2		4–3
16 814.153	−1	6–5	7–6
16 814.157	−1		6–5
16 814.166	1		5–4
19 616.502	0	7–6	8–7
19 616.504	−1		7–6
19 616.510	0		6–5

[a] Experimental uncertainties (1σ) are 1 kHz.
[b] Observed frequency minus that calculated from the least-squares fit. Best fit constants are given in Table III.

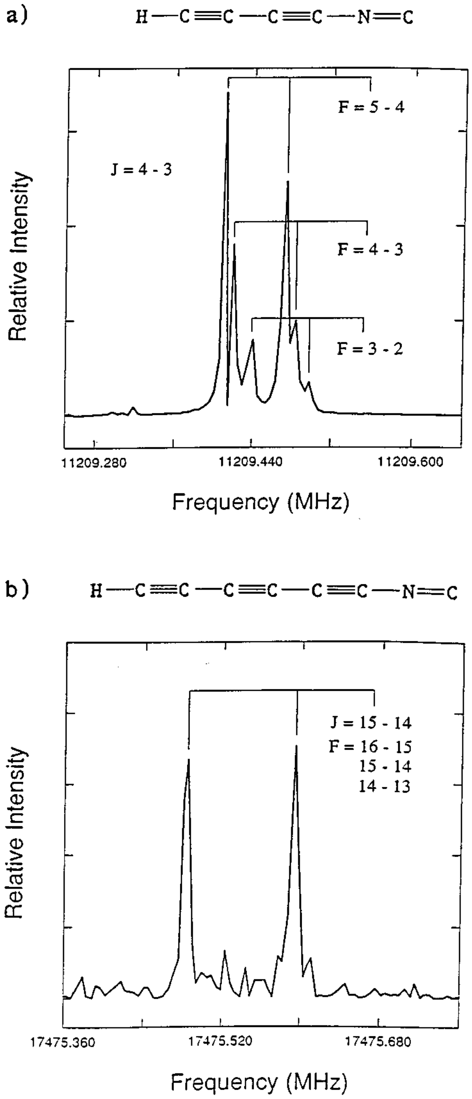

FIG. 2. Sample spectra of the two new isocyanopolyynes. (*Upper*) $J=4\rightarrow 3$ transition of HC_4NC with resolved quadrupole hyperfine structure, and (*lower*) the $J=15\rightarrow 14$ transition of HC_6NC. The observed lines are the result of 2 and 10 min of integration, respectively. Although hyperfine structure is not resolved in HC_6NC owing to the high-J transitions that were measured, the lines are broadened by nearly a factor of 2 beyond the 5 kHz instrumental linewidth. The double-peaked line profile is instrumental in origin—the Doppler splitting that results when a Mach 2 axial molecular beam interacts with the standing wave in the confocal Fabry–Perot cavity of the spectrometer.

TABLE II. Measured rotational transitions of HC_6NC.

Frequency[a] (MHz)	O–C[b] (kHz)	$J'-J$
10 485.350	0	9–8
11 650.385	1	10–9
12 815.420	2	11–10
13 980.447	−3	12–11
15 145.480	0	13–12
16 310.508	−1	14–13
17 475.538	2	15–14

[a] Experimental uncertainties (1σ) are 2 kHz.
[b] Observed frequency minus that calculated from the least-squares fit. Best fit constants are given in Table III.

standard expression for the rotation transition frequencies of a closed-shell linear molecule with quadrupole hyperfine structure (hfs) to the data. As Table III shows, only three constants (B, D, and eQq) were required to fit the HC_4NC data to a rms of less than 2 kHz—one-quarter of the instrumental linewidth, and to the same accuracy HC_6NC was fit with only two, because hfs was not resolved.

The identifications of the two new isocyanopolyynes are quite certain. The rotational constant for HC_4NC of $B_0 = 1401.182\,27(7)$ MHz agrees with the previous theoretical prediction of 1401 ± 7 MHz,[11] which was based on calculations within the coupled electron pair approximation, version 1 (CEPA-1). Likewise, the predicted quartic centrifugal distortion constant of $D_0 = 33 \pm 1$ Hz (note the typographical error in Ref. 11) compares well with the present experimental value of 34.3(9) MHz. Additional support for the correctness of the assignments comes from the extended *ab initio* calculations from this work (see below). For both HC_4NC and HC_6NC, the centrifugal distortion constant, a sensitive measure of size and geometry, is within 10% of that calculated on the assumption that carbon chains behave as classical elastic rods with a Young's modulus independent of length[14] (this model yields an L^{-7} dependence for D and an L^{-4} dependence for D/B). In addition, the identifications pass several standard tests for isocyanopolyynes: (i) The molecules were produced under similar experimental conditions to those that optimize both lines of the shorter member of the series, HC_2NC, and their isomers HC_5N and HC_7N, (ii) they were produced in discharges with different gas mixtures, indicating that the assigned lines do not arise from an impurity, (iii) and hfs was observed in the lighter of the two new molecules, indicating a nitrogen-containing species; the magnitude and sign of the quadrupole coupling constant eqQ is close to the value measured in HC_2NC.[7,8,16] As predicted, the lines we detect also have no appreciable Zeeman effect when a large permanent magnet is brought near the molecular beam, and they are nearly harmonically related by integer quantum members. The absence of lines at subharmonic frequencies rules out larger linear molecules.

Although nitrogen hfs is not observed for HC_6NC, its rotational lines are broadened beyond the intrinsic instrumental 5 kHz linewidth (FWHM). The HC_6NC linewidths are approximately 8 kHz, or nearly twice the linewidth expected from the time of flight of the molecules through the cavity of our spectrometer. If this additional broadening is due to nitrogen hfs, as expected, we estimate $|eQq| \leq 1$ MHz, a value consistent with the quadrupole coupling constant of either HCCNC or HC_4NC.

IV. DETAILS OF *AB INITIO* CALCULATIONS

Following our earlier work on HC_5N[17] and HC_7N,[18] we make use mainly of coupled cluster theory in a rather extensive theoretical investigation of HC_4NC and HC_6NC. The highest level employed corresponds to CCSD(T)[19] and CCSD-T.[20] These variants involve an iterative treatment of the effects of single and double excitation operators (CCSD[21]), and include the effects of connected triple substitutions by means of perturbation theory. Throughout, all valence electrons are correlated in the calculations that were carried out with the MOLPRO suite of programs.[22,23] We mostly employ Dunning's correlation consistent polarized valence triple-zeta (cc-pVTZ) basis set,[24] which comprises 194 contracted Gaussian-type orbitals (cGTOs) for HC_4NC and 254 cGTOs for HC_6NC. In the calculation of equilibrium electric dipole moments, even larger basis sets have been employed. They involve diffuse functions from the "augmented" basis set of the Dunning group.[25] In the post-Hartree–Fock calculations, electric dipole moments are calculated as energy derivatives, e.g., first derivatives of the total energy with respect to the strength of a uniform electric field at zero field strength.

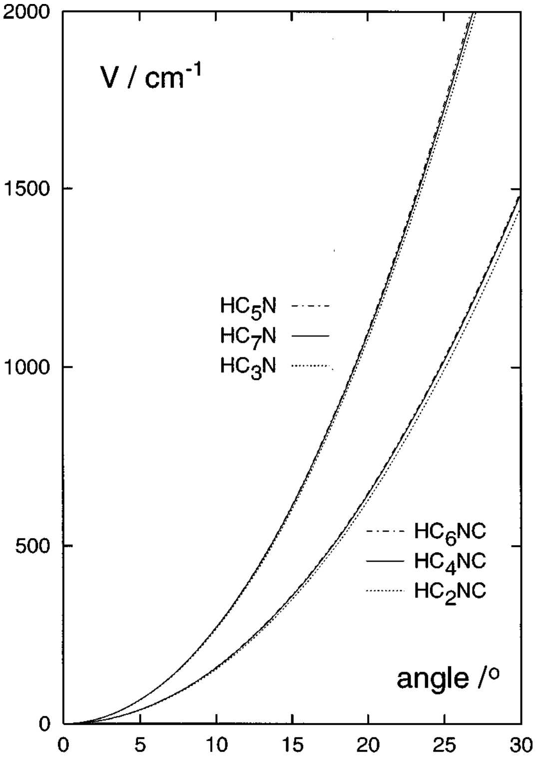

FIG. 3. CNC and CCN bending potentials for isocyanopolyynes and cyanopolyynes, respectively [CCSD(T)/cc-pVTZ results].

Equilibrium geometries for HC_4NC and HC_6NC have been calculated by five different methods: Hartree–Fock self-consistent field (SCF), second-order perturbation theory according to Møller and Plesset (MP2), CCSD, CCSD-T, and CCSD(T). According to our experience, the errors of CCSD-T and CCSD(T) calculations in the equilibrium geo-

TABLE III. Spectroscopic constants of HC_4NC and HC_6NC (in MHz). Uncertainties (in parentheses) are 1σ in the last significant digit.

	HC_4NC		HC_6NC	
Constant	Measured	Expected	Measured	Expected
B	1401.182 27(7)	1401[a]	582.5203(1)	582.4[b]
$D_J \times 10^6$	34.3(9)	33[a]	5.4(3)	4.2[c]
eq$Q$	0.96(2)	0.95[c]	<1.00	0.95[d]

[a] Reference 11.

[b] This work (see the text).

[c] Scaled from the shorter members of the series.

[d] From HC_2NC; see Ref. 16.

TABLE IV. Calculated equilibrium bond lengths (in Å), equilibrium rotational constants, total energies, and equilibrium isomerization energies for HC_4NC.

Method	r_e CH	R_{1e} $C_{(1)}C_{(2)}$	R_{2e} $C_{(2)}C_{(3)}$	R_{3e} $C_{(3)}C_{(4)}$	R_{4e} $C_{(4)}N$	R_{5e} $NC_{(5)}$	B_e (MHz)	V_e (E_h)	ΔE_e (kJ/mol)
CEPA-1[a]	1.0612	1.2120	1.3757	1.2116	1.3174	1.1867	1387.1		116
corr.[a]	1.0616	1.2086	1.3664	1.2082	1.3087	1.1812	1400.7		
SCF[b]	1.0540	1.1827	1.3816	1.1798	1.3105	1.1535	1425.1	−244.277 116	90.0
MP2[b]	1.0625	1.2205	1.3613	1.2219	1.3071	1.1903	1389.9	−245.185 380	136.1
CCSD[b]	1.0623	1.2067	1.3775	1.2056	1.3162	1.1782	1394.3	−245.188 857	112.6
CCSD-T[b]	1.0642	1.2150	1.3732	1.2153	1.3141	1.1875	1386.7	−245.243 889	115.6
CCSD(T)[b]	1.0642	1.2153	1.3733	1.2156	1.3142	1.1880	1386.1	−245.244 905	115.8
corr.[b]	1.0624	1.2089	1.3673	1.2092	1.3082	1.1815	1399.7		

[a] Reference 11.

[b] Basis set: cc-pVTZ (194 cGTOs).

metrical parameters are quite systematic, and predictions of high accuracy (*ca.* 0.0005 Å in equilibrium bond lengths) are feasible on their basis. In this work, we apply the following corrections to the CCSD(T) equilibrium bond lengths: the CH equilibrium bond lengths are reduced by 0.0018 Å, the shorter (acetylenic) CC bond lengths by 0.0064 Å, the longer ones by 0.0060 Å, the CN bonds also by 0.0060 Å, and the isocyanide (NC) bond lengths by 0.0065 Å. The corrections for the first three types of bonds are identical to those employed in our earlier work on HC_5N[17] and HC_7N.[18] The corrections for the CN and NC bonds are taken over from HC_2NC, for which an accurate equilibrium structure was established through a combination of experimental and theoretical data.[26] The CCSD(T)/cc-pVTZ equilibrium structure of HC_2NC has been newly calculated.

A complete CCSD(T) cubic force field was calculated for HC_4NC, thereby enabling the calculation of vibration–rotation coupling constants by standard second-order perturbation theory in normal coordinate space. Therefrom, we get the differences B_0-B_e, which allow for accurate predictions of B_0 values for experimentally unknown isotopic species.

V. RESULTS OF *AB INITIO* CALCULATIONS

A. HC_4NC

All five methods employed [SCF, MP2, CCSD, CCSD-T, and CCSD(T)] yield a linear equilibrium structure for HC_4NC. The calculated equilibrium bond lengths are listed in Table IV along with a corrected equilibrium structure (see Sec. IV) and our earlier predictions.[11] The present corrected equilibrium bond lengths are in very good agreement with our previous corrected values,[11] which were based on the results of CEPA-1 calculations. The largest deviation from the present predictions is only 0.0010 Å and the mean deviation is 0.0006 Å. The present corrected equilibrium geometry yields an equilibrium rotational constant of $B_e = 1399.7$ MHz, 1.5 MHz below the experimental B_0 value (see Table III). A very similar difference of 1.2 MHz was obtained in our earlier study of HC_5N.[17]

According to the present CCSD(T) calculations, the energy minimum of HC_4NC lies higher by $115.8\ \mathrm{kJ\,mol^{-1}}$ compared to HC_5N. Practically, the same value was obtained in our earlier CEPA-1 calculations.[11] While SCF underestimates the equilibrium isomerization energy ΔE_e by $26\ \mathrm{kJ\,mol^{-1}}$, MP2 yields too high a value by $20\ \mathrm{kJ\,mol^{-1}}$. The influence of connected triple substitutions on ΔE_e is minor and amounts to only $3\ \mathrm{kJ\,mol^{-1}}$. Within the harmonic approximation, the CCSD(T) zero-point energies of HC_5N and HC_4NC are 94.9 and $92.9\ \mathrm{kJ\,mol^{-1}}$, so that the energy difference at 0 K is $113.8\ \mathrm{kJ\,mol^{-1}}$.

We have calculated a complete cubic force field for HC_4NC at the CCSD(T) level with the cc-pVTZ basis set. The number of terms is too large to be presented here; a deposit will be made with the electronic Physics Auxiliary Publication Service.[27] The CCSD(T) cubic force field has been employed in the calculation of various spectroscopic constants of HC_4NC, which are listed in Table V. The harmonic vibrational wavenumbers higher than $1000\ \mathrm{cm^{-1}}$ should be accurate to ca. 0.5%, the smaller ones to $5\ \mathrm{cm^{-1}}$. Variational calculations of stretching vibrational transitions and their IR intensities have been previously carried out at the CEPA-1 level,[11] and the ν_1, ν_3, and ν_4 bands of HC_4NC were found to be strongest. The CEPA-1 harmonic bending vibrational wavenumbers differ from the present CCSD(T) values by less than $20\ \mathrm{cm^{-1}}$.

The calculated vibration–rotation coupling constants α_r are of particular interest to the present work. They are expected to be accurate to better than 10%. Analogous calculations for the more stable isomer HC_5N[28] yielded very good agreement with all currently available experimental data. From the calculated α_r values for HC_4NC, we may calculate an approximate value for the difference B_0-B_e via the formula

TABLE V. CCSD(T) spectroscopic constants of HC_4NC.[a]

ω_1	3453	α_1	1.03	q_7^e	0.206
ω_2	2321	α_2	5.11	q_8^e	0.344
ω_3	2163	α_3	3.26	q_9^e	0.376
ω_4	2055	α_4	2.45	q_{10}^e	0.564
ω_5	1202	α_5	3.33	q_{11}^e	1.162
ω_6	626	α_6	1.26	q_7^J	0.090
ω_7	639	α_7	−0.52	q_8^J	−0.043
ω_8	463	α_8	−2.17	q_9^J	−0.057
ω_9	407	α_9	−1.94	q_{10}^J	−0.212
ω_{10}	242	α_{10}	−2.42	q_{11}^J	−0.950
ω_{11}	114	α_{11}	−2.64	D_e	29.53

[a] 194 cGTOs, valence electrons correlated. Harmonic vibrational wavenumbers in $\mathrm{cm^{-1}}$, vibration–rotation coupling constants in MHz, 1-type doubling constants q_t^e in MHz, q_t^J in Hz, equilibrium centrifugal distortion constant in Hz.

$$B_0 - B_e \approx -\sum_i \alpha_i \frac{d_i}{2}, \tag{1}$$

where d_i is the degeneracy factor of vibrational mode i (1 for stretching and 2 for bending modes). The resulting difference is 1.48 MHz. Adding it to the B_e value of the corrected equilibrium structure (Table IV), we arrive at $B_0 = 1401.20$ MHz, in excellent agreement with the present experimental value. This is a clear indication for the quality of the underlying corrected equilibrium structure.

The calculated *l*-type doubling constants q_t^e should be accurate to ca. 5%. Again, the analogous CCSD(T) values for HC_5N[17] agree very well with the available experimental values. An accuracy of *ca.* 10% is expected for the much smaller constants q_t^J, which describe the dependence of *l*-type doubling on the rotational quantum number *J*. The convention of Watson[29] is employed in their definition, which differs in sign from that used by most experimentalists.

The CCSD(T) value for the quartic equilibrium centrifugal distortion constant D_e is 29.5 Hz. A more accurate D_e value, termed $D_e(\text{corr.})$, may be obtained by combining the corrected equilibrium geometry with the CCSD(T) quadratic stretching force constants. The resulting value of $D_e(\text{corr.}) = 30.4$ Hz should be accurate to 1%. The ratio $D_0(\text{exp.})/D_e(\text{corr.})$ of 1.13 appears to be somewhat high since, according to the present *ab initio* calculations, HC_4NC appears to be a rather well-behaved semirigid molecule. It has to be noted that the experimental D_0 value has a relatively large error (see Table III). 3σ, which is a realistic measure of the uncertainty of the measurements—systematic errors not being taken into account—is as large as 2.7 Hz. Therefore, a more accurate prediction of $D_0(HC_4NC)$ should be possible by a suitable scaling procedure. In this work, three different procedures are employed. The first one makes use of a scaling factor taken over from HC_2NC, which amounts to 1.059. In this way we arrive at a D_0 prediction of 32.2 Hz. A second scaling factor is obtained by comparison of the experimental D_0 value for HC_5N[30] and $D_e(\text{corr.}) = 27.9$ Hz from our recent theoretical work.[17,28] The scaling factor is now 1.079 so that $D_0(HC_4NC) = 32.8$ Hz results. We may also make use of the very recent experimental D_0 value for NC_3NC,[31] which has a slightly more shallow CNC bending potential than HC_4NC. This yields $D_0(HC_4NC) = 33.0$ Hz, which is probably our most reliable prediction. Its uncertainty is believed to be smaller than 3%.

TABLE VI. B_0 predictions for less abundant isotopomers of HC_4NC.

Isotopomer	B_0 (MHz)	Isotopomer	B_0 (MHz)
DCCCCNC	1336.050	$HCCC^{13}CNC$	1399.620
$H^{13}CCCCNC$	1364.012	$HCCCC^{15}NC$	1386.906
$HC^{13}CCCNC$	1386.825	$HCCCCN^{13}C$	1364.691
$HCC^{13}CCNC$	1399.886		

We may make use of the present accurate equilibrium structure, the calculated vibration–rotation coupling constants [via Eq. (1)] and the experimental B_0 value for the most abundant species in order to arrive at rather accurate B_0 predictions for the less abundant isotopomers (*). They are calculated according to the formula

$$B_0^* = \left(B_e^* - \sum_i \alpha_i^* \frac{d_i}{2} \right) \cdot F, \tag{2}$$

where the scaling factor F has a value of 0.999 986 7. B_0 predictions for seven different isotopomers of HC_4NC are listed in Table VI. According to our recent experience with NC_3NC,[31] the B_0 values for ^{13}C and ^{15}N substituted species should be accurate to ca. 0.005 MHz. The B_0 value for DC_4NC may be somewhat less precise.

Calculated equilibrium dipole moments for HC_4NC are listed in Table VII. A variety of basis sets is employed which range in size from 147 to 299 cGTOs. Throughout, the calculations are carried out at the recommended equilibrium geometry from this work. The basis set dependence is rather minor. On the other hand, electron correlation effects play an important role. The CCSD(T) value obtained with the largest basis is larger than the corresponding SCF value by as much as 0.747 D or 30%. The former value of −3.253 D should be accurate to 0.01 D. It differs from our previous CEPA-1 value[11] by 2%. MP2 significantly overestimates the correlation effect.

B. HC_6NC

Calculated equilibrium bond lengths for HC_6NC are listed in Table VIII. Again, the corrected values should be

TABLE VII. Equilibrium dipole moment (in D) of HC_4NC.[a]

Method	147 cGTOs[b]	194 cGTOs[c]	205 cGTOs[d]	247 cGTOs[e]	299 cGTOs[f]
SCF	−2.559	−2.521	−2.534	−2.506	−2.506
MP2	−3.600	−3.581	−3.608	−3.609	−3.601
CCSD	−3.137	−3.113	−3.150	−3.141	−3.133
CCSD-T	−3.244	−3.224	−3.263	−3.259	−3.250
CCSD(T)	−3.246	−3.226	−3.265	−3.262	−3.253

[a] All calculations are carried out at the recommended equilibrium structure from this work. The sign convention is such that the negative end of the dipole is located at the terminal carbon site.

[b] The cc-pVTZ basis exclusive of *f* functions at C and N and of *d* functions at H.

[c] Full cc-pVTZ basis.

[d] The s,p,d (C,N) and s,p (H): aug-cc-pVTZ.

[e] Full cc-pVTZ basis for C and N plus diffuse (s,p,d) functions from an aug-cc-pVTZ set; basis for H; (s,p) from an aug-cc-pVTZ set.

[f] Full aug-cc-pVTZ basis.

TABLE VIII. Calculated equilibrium bond lengths (in Å), equilibrium rotational constants, total energies, and equilibrium isomerization energies for HC_6NC.[a]

Method	r_e (CH)	R_{1e} $C_{(1)}C_{(2)}$	R_{2e} $C_{(2)}C_{(3)}$	R_{3e} $C_{(3)}C_{(4)}$	R_{4e} $C_{(4)}C_{(5)}$	R_{5e} $C_{(5)}C_{(6)}$	R_{6e} $C_{(6)}N$	R_{7e} $NC_{(7)}$	B_e (MHz)	V_e (E_h)	ΔE_e (kJ/mol)
SCF	1.0548	1.1806	1.3744	1.1835	1.3703	1.1792	1.3093	1.1516	593.4	−319.981 379	88.5
MP2	1.0628	1.2215	1.3593	1.2302	1.3529	1.2238	1.3056	1.1908	577.9	−321.182 948	136.6
CCSD	1.0629	1.2078	1.3746	1.2121	1.3704	1.2071	1.3148	1.1788	579.2	−321.180 029	112.0
CCSD-T	1.0646	1.2162	1.3713	1.2225	1.3661	1.2171	1.3126	1.1883	576.1	−321.254 877	114.8
CCSD(T)	1.0646	1.2165	1.3714	1.2228	1.3663	1.2174	1.3127	1.1887	575.9	−321.256 199	115.0
corr.	1.0628	1.2101	1.3654	1.2164	1.3603	1.2110	1.3067	1.1822	581.5		

[a] Basis set: cc-pVTZ (254 cGTOs).

accurate to *ca.* 0.0005 Å and will be taken as reference values in the following discussion. The distances r_e and $R_{1e} - R_{4e}$ differ only marginally from those of HC_7N.[18] A slightly larger difference of 0.0037 Å is observed for R_{5e}. The CN and NC equilibrium bond lengths show differences of −0.0072 and 0.0028 Å from those of the mixed experimental/theoretical structure for HC_2NC.[26] The equilibrium rotational constant of HC_6NC as calculated from the recommended equilibrium structure is $B_e = 581.5$ MHz. It is smaller than the experimental B_0 value (see Table III) by 1.0 MHz. A very similar difference of 0.9 MHz was recently obtained for HC_7N.[18] The latter value was used in a B_0 prediction for HC_6NC of 582.4 ± 0.5 MHz which proved to be useful in the assignment of the microwave lines.

According to the present CCSD-T and CCSD(T) calculations, the HC_6NC isomer has its minimum on the common potential energy hypersurface at an energy $115\ \mathrm{kJ\ mol^{-1}}$ higher than HC_7N. Electron correlation effects make up $26.5\ \mathrm{kJ\ mol^{-1}}$ of this difference. It is overestimated by $22\ \mathrm{kJ\ mol^{-1}}$ when electron correlation is taken into account by MP2.

For economical reasons, the vibrations of HC_6NC have been treated within the harmonic approximation. The CCSD(T) harmonic stretching vibrational wavenumbers (in $\mathrm{cm^{-1}}$) are 3454, 2312, 2262, 2122, 2057, 1307, 930, and 470. The corresponding values for HC_7N[18] are 3453, 2304, 2260, 2181, 2081, 1285, 900, and 463.

Since CCSD(T) calculations with the cc-pVTZ basis set for bent nuclear configurations of HC_6NC are rather time consuming, we have employed a mixed procedure whereby the diagonal quadratic bending force constants are calculated by CCSD(T) and the less important off-diagonal terms by MP2. In both cases the CCSD(T) equilibrium structure is taken as the reference geometry for the calculation of the bending force constants. The results are given in Tables IX and X. The former table also contains values obtained by SCF, CCSD, and CCSD-T. Comparable data for HC_7N are given in Ref. 18. As expected, the most significant difference between HC_6NC and HC_7N is in the bending potential $V(\eta)$ which describes either CNC or CCN bending. $V(\eta)$ is considerably more shallow in HC_6NC. As is illustrated in Fig. 3, the CCSD(T) CNC bending potentials are very similar in the series of the isocyanopolyynes $HC_{2n}NC$ $(n = 1-3)$. A similar situation holds for the steeper CCN bending potentials of the cyanopolyynes. Our calculations for bent nuclear configurations of both isocyanopolyynes and cyanopolyynes are not indicative of any unusual anharmonicity effects on the vibrational states, and we believe that both species behave like usual semirigid linear molecules.

The harmonic bending vibrational wavenumbers for HC_6NC, as obtained by the combination of diagonal CCSD(T) and off-diagonal MP2 force constants are (in $\mathrm{cm^{-1}}$): 631, 503, 458, 403, 262, 163, and 64. The corresponding values for HC_7N (see Table 8 of Ref. 18) are 650, 522, 503, 450, 280, 163, and 62.

Due to the similarity of the vibrational modes, the harmonic approximation should yield high accuracy for the difference in the zero-point vibrational energies of the two isomers. It is as small as $1.8\ \mathrm{kJ\ mol^{-1}}$ and is thus of little significance.

The CCSD(T) quartic centrifugal distortion constant for HC_6NC is 3.78 Hz; the corresponding value obtained with the corrected equilibrium geometry is $D_e(\mathrm{corr.}) = 3.89$ Hz. In an analogous way, a $D_e(\mathrm{corr.})$ value of 3.65 Hz is obtained for HC_7N. The ratio $D_0(\mathrm{exp.})/D_e(\mathrm{corr.})$ for the more stable isomer is thus 1.047, taking the experimental value of $D_0(HC_7N) = 3.821 \pm 0.087$ Hz from the work of Kirby, Kroto, and Walton.[32] The appropriate scaling factor for HC_6NC may be somewhat higher but it is improbable that it significantly exceeds 1.10. Our recommendation for $D_0(HC_6NC)$ is thus 4.2 ± 0.1 Hz. It is slightly outside three times the standard deviation of the present experimental value (cf. Table III).

Calculated equilibrium dipole moments μ_e for HC_6NC are listed in Table XI. Four different basis sets are employed. The largest one, which comprises 330 cGTOs, is very flexible and, at the CCSD-T or CCSD(T) level of theory, should yield μ_e values accurate to *ca.* 0.01 D. Electron correlation effects make a very substantial contribution to μ_e of 43%. Again, MP2 yields a relatively poor value for μ_e.

VI. DISCUSSION

We have estimated the abundances of HC_4NC and HC_6NC in our molecular beam, and the detection limit that we can achieve with our FTM spectrometer. The largest uncertainty is in the estimation of the divergence of the supersonic expansion, and thus the fraction of molecules in the beam waist (the distance from the center of the cavity to the 1/*e* points of the field strength) of the confocal mode in the Fabry–Perot cavity. From model calculations, this fraction is probably uncertain to a factor of at least 2. Correcting the line intensities for the rotational partition function and dipole moments probably contributes an additional factor of 2 un-

TABLE IX. Diagonal quadratic bending force constants for HC_6NC[a] (in a.u.).

Force constant[b]	SCF	MP2	CCSD	CCSD-T	CCSD(T)
α^2	0.036 497	0.025 233	0.027 372	0.025 128	0.025 103
β^2	0.048 173	0.041 523	0.041 447	0.040 154	0.040 134
γ^2	0.046 906	0.039 089	0.040 266	0.038 243	0.038 223
δ^2	0.045 494	0.036 516	0.038 208	0.036 318	0.036 296
ϵ^2	0.045 496	0.040 038	0.039 694	0.038 060	0.038 024
ζ^2	0.050 982	0.034 701	0.039 039	0.035 874	0.035 819
η^2	0.021 470	0.027 652	0.023 350	0.023 791	0.023 718

[a] Evaluated around the CCSD(T) equilibrium geometry. Basis set: cc-pVTZ (254 cGTOs).

[b] Notation α^2 corresponds to $\frac{1}{2}(\partial^2 V/\partial\alpha^2)_{\rm ref}$, where α is the HCC angle.

certainty. Based on measurements of the intensities of the rare isotopic species of OCS and HC_3N (e.g., $^{18}OC^{34}S$, $HC_3\,^{15}N$, etc.) in a dilute sample of HC_3N in Ar and a calibrated sample of dilute OCS in Ar, we estimate that there are $\leqslant 7\times 10^{10}$ HC_4NC and $\leqslant 2\times 10^{10}$ HC_6NC molecules per gas pulse in our molecular beam, the upper limit calculated on the assumption that all the molecules are in the beam waist; if the fraction is closer to 0.1, as we estimate, each of these limits should be reduced by an order of magnitude.

The minimum OCS abundance that can be detected with our FTM spectrometer is $\leqslant 3\times 10^9$ molecules per gas pulse, assuming 3 h of integration, the fraction of molecules in the beam waist is unity, and the rotational temperature is 2.5 K, at which $T_{\rm rot}$ one-third of the rotational population is in the $J=0$ level. At 10 GHz, the beam waist is about 6 cm, which corresponds to an active volume of about $1000\ {\rm cm}^3$, or a number density of $\leqslant 3\times 10^6$ OCS molecules/$\rm cm^3$ in the center of the Fabry–Perot cavity during a pulse. Near the throat of the supersonic expansion where the number density approaches 10^9 molecules/$\rm cm^3$, the two new isocyanopolyynes and many of our other new carbon chains might be detected by modern laser techniques, such as laser-induced fluorescence for transitions that fluoresce, or resonant-enhanced ionization multiphoton ionization for those that do not, since the threshold for laser detection by either technique is several orders of magnitude lower than FTM spectroscopy, typically $10^5\ {\rm cm}^{-3}$ or less.[33]

The detection of HC_4NC and HC_6NC demonstrates that it is possible to observe fairly energetic isomers of long carbon chains. Although these isocyanopolyynes are calculated to be $114\ {\rm kJ\ mol}^{-1}$ less stable than HC_5N and HC_7N, they are evidently produced in our laboratory discharges in sufficient abundance to be observed by FTM spectroscopy. With the production techniques we have developed, other isomers, including other linear structures, or even nonlinear ones, may be detectable with our present spectrometer. In a closely related series, the C_nN radicals, for example, recent theoretical calculations by Bettinger and Schleyer[34] conclude that monocyclic c-C_9N is only about $100\ {\rm kJ\ mol}^{-1}$ less stable than linear C_9N, the implication being that at modest chain lengths fairly energetic molecular isomers with exotic geometric structures may be observable. With increasing chain length, monocyclic rings or other ring isomers may even compete with the linear form for the ground state, since beyond a critical size range the stability of forming an additional bond is greater than that lost from ring strain.

The two isocyanopolyynes here are both candidates for astronomical detection, because the first two members of the series (HNC and HC_2NC) have already been observed in the rich molecular cloud TMC-1, one of the best carbon chains sources so far discovered. HC_4NC and HC_6NC also have large equilibrium dipole moments (-3.25 and -3.49 D, respectively, for HC_4NC and HC_6NC), making them easier to detect than long carbon molecules. In TMC-1, if the intensity decrement on ascending the cyanopolyyne series holds for the isocyanopolyynes, lines of HC_4NC should be detectable at the 10 mK level because HC_2NC ($T\approx 500$ mK) is strong there.[5] With the spectroscopic constants in Table III, the astronomically most interesting lines of both chains can now

TABLE X. MP2 Off-diagonal quadratic bending force constants for HC_6NC.[a]

Force constant	Value (a.u.)	Force constant	Value (a.u.)
$\alpha\beta$	0.022 35	$\gamma\delta$	0.023 40
$\alpha\gamma$	−0.002 85	$\gamma\epsilon$	−0.004 86
$\alpha\delta$	−0.001 10	$\gamma\zeta$	−0.001 99
$\alpha\epsilon$	−0.000 23	$\gamma\eta$	0.000 01
$\alpha\zeta$	0.000 09	$\delta\epsilon$	0.001 50
$\alpha\eta$	−0.000 04	$\delta\zeta$	−0.003 72
$\beta\gamma$	−0.000 64	$\delta\eta$	−0.000 01
$\beta\delta$	−0.004 74	$\epsilon\zeta$	0.029 84
$\beta\epsilon$	0.001 24	$\epsilon\eta$	−0.002 30
$\beta\zeta$	0.000 25	$\zeta\eta$	0.004 60
$\beta\eta$	0.000 01		

[a] Evaluated around the CCSD(T) equilibrium geometry. Basis set: cc-pVTZ (254 cGTOs).

TABLE XI. Equilibrium dipole moment (in *D*) of HC_6NC.[a]

Method	193 cGTOs[b]	254 cGTOs[c]	269 cGTOs[d]	330 cGTOs[e]
SCF	−2.683	−2.636	−2.651	−2.620
MP2	−3.902	−3.879	−3.905	−3.895
CCSD	−3.343	−3.314	−3.354	−3.336
CCSD-T	−3.482	−3.456	−3.497	−3.483
CCSD(T)	−3.482	−3.459	−3.501	−3.487

[a] All calculations are carried out at the recommended equilibrium structure from this work.

[b] The cc-pVTZ basis exclusive of *f* functions at C and N and of *d* functions at H.

[c] Full cc-pVTZ basis.

[d] The s,p,d (C,N) and s,p (H); aug-cc-pVTZ.

[e] Full cc-pVTZ basis for C and N plus diffuse (s,p,d) functions from the aug-cc-pVTZ set; basis for H: (s,p) from the aug-cc-pVTZ set.

be predicted to high precision (better than $1\,\mathrm{km\,s^{-1}}$ in equivalent radial velocity), allowing astronomical searches to be conducted with confidence. Astronomical detection of molecular isomers longer than HC_3N would be useful, both to provide additional tests of chemical processes in space and the importance of specific ion–molecule reactions in the formation mechanisms of cyano- and isocyanopolyynes.[35]

ACKNOWLEDGMENTS

Thanks are due to Professor H.-J. Werner (University of Stuttgart) and Professor P. J. Knowles (University of Birmingham) for providing us with a copy of MOLPRO96. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Carl A. Gottlieb for helpful comments.

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