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M. C. McCarthy, A. J. Apponi, V. D. Gordon, C. A. Gottlieb, P. Thaddeus, T. Daniel Crawford, and John F. Stanton



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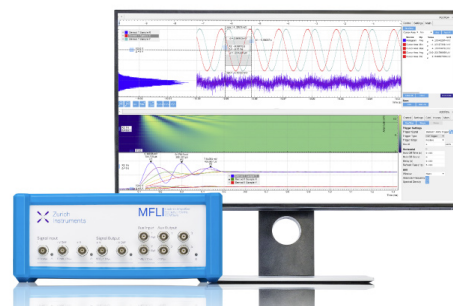
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Rotational spectrum and theoretical structure of the carbene HC₄N

M. C. McCarthy,^{a)} A. J. Apponi, V. D. Gordon, C. A. Gottlieb, and P. Thaddeus

Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138

and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

T. Daniel Crawford and John F. Stanton

Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas,

Austin, Texas 78712-1167

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Following a high-level coupled cluster calculation, the rotational spectrum of the bent HC₄N singlet carbene was detected in a supersonic molecular beam by Fourier transform microwave spectroscopy. The three rotational constants, the leading centrifugal distortion constants, and two nitrogen hyperfine coupling constants were determined to high accuracy. The rotational constants agree with those calculated *ab initio* to better than 0.5%. Like the isoelectronic C₅H₂ carbene of similar structure, HC₄N was found to have fairly large centrifugal distortion and a large inertial defect. The calculated dipole moment of HC₄N is 2.95 D. © 1999 American Institute of Physics. [S0021-9606(99)00339-6]

I. INTRODUCTION

Recent gas-phase ion mobility studies of carbon suggest the presence of many isomers in the transition region from chains to rings and to larger clusters including fullerenes.¹ Few reactive carbon molecules other than linear chains have been observed to date by high-resolution spectroscopy, but laboratory detection of many fairly energetic isomers may now be possible by means of rotational spectroscopy applied to a supersonic molecular beam. With high-level *ab initio* calculations as a guide, laboratory detection of many new carbon clusters in various isomeric arrangements should be possible.

HC₄N represents one of the simplest molecular systems which is calculated to possess several low-lying, highly polar carbene isomers.² Carbene isomers are of interest to chemists, in part, because knowledge of their rotational spectra provides new information on the electronic structure, chemical bonding, and molecular geometry of small reactive carbon molecules, and provides precise tests of quantum chemical calculations. Isomers of HC₄N are also good candidates for detection in space with radio telescopes, because more than 40 nitrogen-containing molecules have been identified in the interstellar gas and in circumstellar shells. Astronomical detection of HC₄N is facilitated by the large permanent electric dipole moment of the nitrile group.

This paper describes a joint experimental and theoretical investigation of the HC₄N isomer with the bent backbone shown in Fig. 1. The experimental work was done at Cambridge with a Fourier transform microwave (FTM) spectrometer, and the theoretical work at Austin using coupled cluster methods. Singlet HC₄N is isoelectronic with a C₅H₂ isomer with the same planar, bent carbene structure (see isomer 7 of Refs. 3 and 4); a molecule which also is highly polar and

whose rotational spectrum is also that of a nearly symmetric prolate top.

II. THEORETICAL

The molecular properties of bent HC₄N were computed using coupled cluster methods with three different basis sets. A summary of these calculations is given in Table I. The smallest basis set, denoted DZP, consists of Dunning's contractions⁵—(9s5p)/[4s2p] for carbon and nitrogen and (4s)/[2s] for hydrogen—of Huzinaga's primitive Gaussian basis sets⁶ with a set of polarization functions on each atom.⁷ The second basis set, denoted TZ2P, consists of Dunning's contractions⁸—(10s6p)/[5s3p] for carbon and nitrogen and (5s)/[3s] for hydrogen—of Huzinaga's primitive Gaussian basis sets⁶ with two sets of polarization functions on each atom.⁹ The largest basis set is Dunning's standard correlation-consistent, polarized-valence, triple-zeta basis set (cc-pVTZ)¹⁰ using a (10s5p2d1f)/[4s3p2d1f] contraction for carbon and nitrogen and a (5s2p1d)/[3s2p1d] contraction for hydrogen. Pure angular momentum functions were used for all *d*- and *f*-type orbitals.

The coupled cluster methods employed in this work include the conventional singles and doubles model (CCSD)¹¹ based on a spin-restricted, closed-shell Hartree-Fock reference determinant, as well as CCSD augmented with a perturbative estimate of the effects of connected triple excitations [CCSD(T)].^{12,13} Geometry optimizations were carried out with analytic energy gradients for the CCSD and CCSD(T) methods.^{14,15} The optimizations were considered to have converged once the root-mean-square of the internal coordinate forces fell below a threshold of $1.0 \times 10^{-5} E_h/a_0$. All computations were carried out with the ACESII package of quantum chemical programs.¹⁶

^{a)}Electronic mail: mccarthy@cfa.harvard.edu

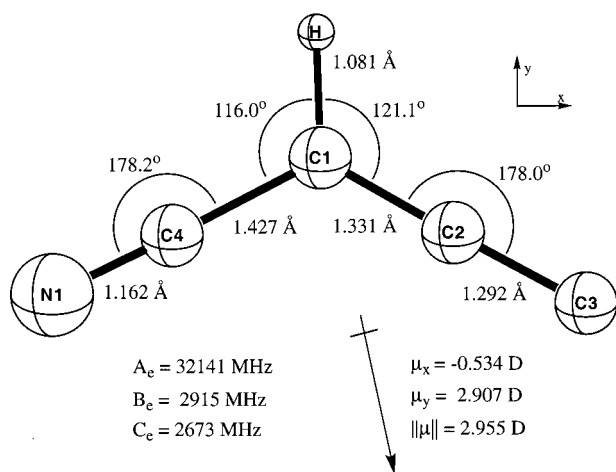


FIG. 1. Structure and dipole moment of the lowest $1A'$ state of the bent isomer of HC₄N as determined at the cc-pVTZ/CCSD(T) level of theory.

III. EXPERIMENT

The rotational spectrum of bent HC₄N was detected in a supersonic molecular beam by FTM spectroscopy¹⁷ with an improved version of the reactive molecule spectrometer¹⁸ recently used to detect and characterize rotational spectra of a ring-chain isomer of HC₄N¹⁹ and four isomers of the isoelectronic carbene C₅H₂.²⁰ This spectrometer now operates from 5 to 43 GHz and is fully computer controlled so that automated scans covering wide frequency bands and requiring many hours of integration are readily conducted. For highest sensitivity, the mirrors of the Fabry–Perot and first-stage amplifier are cooled to the temperature of liquid nitrogen, thereby reducing the system noise temperature to about 200 K—nearly a factor of 4 higher sensitivity than at room temperature. By means of separate antennas tuned externally and independently for microwave drive and detection, optimal coupling of the microwave power into and out of the Fabry–Perot cavity of the spectrometer is achieved over much of the

centimeter-wave band. Operational efficiency and system performance have also been improved with the addition of a gate valve assembly that allows the axially oriented discharge nozzle to be removed and serviced even when the spectrometer is working at 77 K.

The conditions for optimal production of bent HC₄N were nearly identical to those which yield the strong lines of the ring-chain isomer:¹⁹ a low-current dc discharge (900 V) synchronized with a 150 μ s long gas pulse at a total pressure behind the nozzle of 2 atm. The strongest lines of bent HC₄N were obtained with a dilute mixture (0.2%) of HC₃N in Ne. Lines of HC₄N were also produced with two other gas mixtures: diacetylene and methylcyanoacetylene (0.5% each) in Ne, and diacetylene and cyanogen (0.5% each) in Ne, with no significant improvement in line intensities.

Under the best conditions, the intensities of the strongest lines of bent HC₄N are about nine times weaker than those of the ring-chain, which is calculated by Aoki *et al.*² to be the most stable singlet isomer. For isoelectronic C₅H₂, a similar intensity ratio of about 7 was observed. From its line intensities relative to those of the rare isotopic species of OCS in a calibrated (1%) sample diluted in Ne, we estimate the abundance of bent HC₄N to be $\sim 10^{11}$ molecules per gas pulse.

IV. DATA AND ANALYSIS

The observed rotational transitions of bent HC₄N are indicated in Fig. 2; the measured laboratory frequencies between 10 and 40 GHz are given in Table II, and a typical hyperfine triplet is shown in Fig. 3. Spectroscopic constants were determined by fitting a theoretical spectrum calculated from the standard asymmetric-top Hamiltonian²¹ to the measured frequencies. As Table III shows, eight parameters—the three rotational constants, three centrifugal distortion constants, and two quadrupole coupling constants—are required to fit the data to an rms of less than 2 kHz. Since both *a*- and *b*-type rotational transitions were observed, all three rota-

TABLE I. Coupled cluster predictions of structural data for the ground state of bent HC₄N. Bond lengths in angstroms, angles in degrees, rotational constants in MHz, and dipole moments in Debye, where the components and signs of the dipole moment correspond to the molecule lying in the *xy*-plane as depicted in Fig. 1. The positive *y*- and *x*-axes are to the top and right of the figure, respectively.

	DZP/CCSD	DZP/CCSD(T)	TZ2P/CCSD	cc-pVTZ/CCSD(T)
$r(\text{H}-\text{C}_1)$	1.094	1.096	1.082	1.081
$r(\text{C}_1-\text{C}_2)$	1.346	1.356	1.327	1.331
$r(\text{C}_2-\text{C}_3)$	1.314	1.318	1.292	1.292
$r(\text{C}_1-\text{C}_4)$	1.453	1.451	1.439	1.427
$r(\text{C}_4-\text{N})$	1.174	1.181	1.155	1.162
$\theta(\text{H}-\text{C}_1-\text{C}_2)$	121.4	121.5	121.3	121.1
$\theta(\text{H}-\text{C}_1-\text{C}_4)$	116.3	116.3	116.2	116.0
$\theta(\text{C}_1-\text{C}_2-\text{C}_3)$	177.7	177.6	178.5	178.0
$\theta(\text{C}_1-\text{C}_4-\text{N})$	178.3	178.4	178.0	178.2
A_e	30784	30414	31527	32141
B_e	2848	2832	2927	2915
C_e	2607	2590	2679	2673
μ_x	-0.245	-0.431	-0.303	-0.534
μ_y	2.871	2.876	2.940	2.906
$\ \mu\ $	2.881	2.908	2.956	2.955

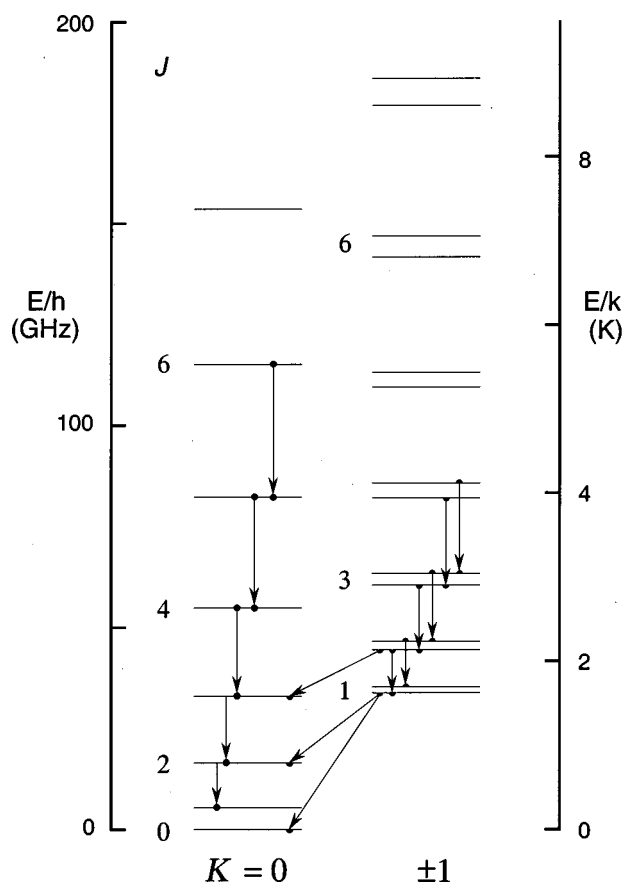


FIG. 2. Lower rotational levels of bent HC₄N. Arrows indicate the rotational transitions measured, each of which has resolved quadrupole hyperfine structure from the nitrogen nucleus.

tional constants are determined to high accuracy. The entire radio spectrum of HC₄N can now be predicted accurately from the microwave to the far infrared.

The identification of bent HC₄N is quite certain. As Table III shows, the rotational constants are within 0.5% of those predicted from the *ab initio* structure, and this agreement alone makes it highly unlikely that the assignment is wrong. There is additional evidence that we are observing the claimed isomer and no other molecule: (i) the *A* rotational constant, a sensitive measure of the molecular geometry, is within 0.6% to that found for the analogous isomer of C₅H₂; (ii) the three centrifugal distortion constants are very close to those found for bent C₅H₂;²⁰ and (iii) the quadrupole hyperfine coupling constants χ_{aa} and $(\chi_{bb} - \chi_{cc})$ agree fairly well with those of other molecules with a terminal CN group (on the assumption that the CN bond is rotated 26° with respect to the *a*-inertial axis; see Fig. 1). As predicted for a singlet carbene, the lines we assign have no appreciable Zeeman effect when a strong permanent magnet is brought near the supersonic beam, and the lines are nearly harmonic in frequency. Finally, the harmonic defect is much larger than that expected from centrifugal distortion alone, but is close to that expected for a molecule with a bent carbon backbone.

V. DISCUSSION

Large centrifugal distortion is encountered in bent HC₄N, as in the structurally similar isomer of C₅H₂. Unlike

TABLE II. Measured rotational transitions of bent HC₄N.

Transition			Frequency ^a (MHz)	O - C ^b (kHz)
$J'_{K'_a, K'_c} \rightarrow J_{K_a, K_c}$	Type	$F' \rightarrow F$		
$2_{1,2} \rightarrow 1_{1,1}$	<i>a</i>	2 → 1	10 968.319	1
		3 → 2	10 969.360	-1
$2_{0,2} \rightarrow 1_{0,1}$	<i>a</i>	2 → 2	11 216.313	0
		1 → 0	11 216.480	-1
		2 → 1	11 217.297	1
		3 → 2	11 217.371	1
		1 → 1	11 218.940	-1
$2_{1,1} \rightarrow 1_{1,0}$	<i>a</i>	2 → 1	11 468.995	0
		3 → 2	11 469.988	-2
$2_{1,2} \rightarrow 3_{0,3}$	<i>b</i>	2 → 2	11 982.992	1
		3 → 4	11 984.272	-1
		1 → 2	11 984.386	0
		2 → 3	11 984.476	-2
		3 → 3	11 985.374	0
$3_{1,3} \rightarrow 2_{1,2}$	<i>a</i>	3 → 2	16 452.424	0
		2 → 1	16 452.656	1
		4 → 3	16 452.732	0
$3_{0,3} \rightarrow 2_{0,2}$	<i>a</i>	3 → 3	16 820.761	-4
		2 → 1	16 821.664	0
		3 → 2	16 821.822	0
$3_{1,2} \rightarrow 2_{1,1}$	<i>a</i>	4 → 3	16 821.864	-2
		3 → 2	17 203.385	-1
		4 → 3	17 203.668	2
$1_{1,1} \rightarrow 2_{0,2}$	<i>b</i>	2 → 1	17 203.732	0
		0 → 1	17 835.971	1
		1 → 1	17 836.337	0
		2 → 3	17 836.778	0
		2 → 2	17 837.837	2
$4_{1,4} \rightarrow 3_{1,3}$	<i>a</i>	1 → 2	17 837.980	-2
		4 → 3	21 934.758	0
		3 → 2	21 934.822	-1
$4_{0,4} \rightarrow 3_{0,3}$	<i>a</i>	5 → 4	21 934.900	1
		3 → 2	22 421.344	1
		4 → 3	22 421.406	0
		5 → 4	22 421.438	1
		4 → 3	22 935.922	2
$4_{1,3} \rightarrow 3_{1,2}$	<i>a</i>	3 → 2	22 936.031	-3
		5 → 4	22 936.045	2
		4 → 3	28 014.383	0
$5_{0,5} \rightarrow 4_{0,4}$	<i>a</i>	5 → 4	28 014.413	1
		6 → 5	28 014.438	0
		5 → 4	33 599.209	-4
$6_{0,6} \rightarrow 5_{0,5}$	<i>a</i>	6 → 5	33 599.230	4
		7 → 6	33 599.248	-1
		0 → 1	34 663.564	-1
		2 → 1	34 663.787	1
		1 → 1	34 663.934	2

^aExperimental uncertainties (1 σ) are 1 kHz.

^bObserved frequency minus that calculated from the least-squares fit. Best fit constants are given in Table III.

other nearly prolate symmetric tops, which have recently been studied by the present technique, both chains require a third fourth-order distortion constant, δ_J , to reproduce the centimeter-wave spectra. When this constant is varied for bent HC₄N, Δ_J converges to a value five times larger than that found for the HC₄N ring-chain. The converged value is quite similar to that found for bent C₅H₂, and Δ_{JK} is again negative. Since the carbon chain backbone is bent 57° from linearity, the large centrifugal distortion may simply reflect the increased effect of low-lying bending modes when the

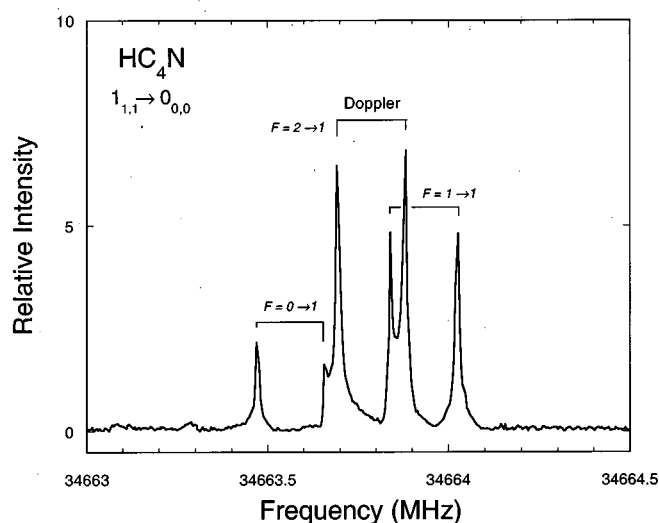


FIG. 3. Sample spectrum of HC₄N showing nitrogen quadrupole hyperfine structure. The double-peaked line profile is instrumental in origin—the Doppler splitting that results when a Mach 2 axial molecular beam interacts with the standing wave in the confocal Fabry–Perot cavity of the spectrometer.

chain backbone is significantly displaced from the *a*-inertial axis. Indeed, analytic harmonic vibrational frequency calculations^{22,23} at the DZP/CCSD level of theory predict two low-lying bending frequencies at 130 cm^{−1} (in-plane) and 216 cm^{−1} (out-of-plane). In addition, DZP/CCSD centrifugal distortion constants corresponding to the *A*-reduced representation calculated from the corresponding quadratic force constants are (in MHz): $\Delta_J = 0.001\,46$, $\Delta_{JK} = -0.129$, and $\delta_J = 0.000\,368$, in reasonable agreement with the experimental data.²⁴

With the spectroscopic constants listed in Table III, precise frequencies for the most likely astronomical rotational lines of HC₄N at frequencies below 150 GHz can be calculated to better than 1 km s^{−1} in equivalent radio velocity; deliberate searches with radio telescopes can therefore be undertaken. The *b*-type transitions will be more than 25 times more intense than the *a*-type transitions owing to the large component of the dipole moment along the *b*-inertial axis (2.91 D versus −0.53 D along the *a*-axis). Although HC₄N is quite light, the strongest *b*-type transitions will tend

to lie at fairly low frequency (i.e., <20 GHz) in a warm source such as IRC+10216—a frequency range where there are presently few published surveys. In the spectral line surveys of astronomical sources which have been published, there is no evidence for HC₄N. For example, in the extensive survey of IRC+10216 by Kawaguchi *et al.*,²⁵ the 1_{1,1}–0_{0,0} line at 34663.8 MHz does not appear at the 10 mK level. Searches at exact frequencies for this and other *b*-type transitions with existing radio telescopes could probably improve current detection limits by a factor of about 3; with larger radio telescopes that will soon be in operation, a factor of 5 improvement may be possible.

Other isomers of HC₄N are now good candidates for laboratory detection. One of the most interesting candidates is a linear triplet chain calculated to lie 0.3 eV above ground.² This chain is similar to triplet HCCN, which has been detected both in the laboratory²⁶ and in space.²⁷ Although microwave detection of triplet HC₄N will be difficult owing to the large expected spin–spin interaction, the central fine structure component should be recognizable as a nearly harmonic series of magnetic lines related in frequency by integer quantum numbers. A similar approach was recently used to detect the central component of SiC₃, SiC₅, and SiC₇ in their ³Σ ground states.²⁸

The laboratory detection here of a fairly energetic isomer of HC₄N following a high-level *ab initio* calculation is a specific example of how the close coordination of theoretical calculations and laboratory techniques can be used to detect reactive molecules of chemical and astronomical interest. Theoretical calculations are clearly desirable prior to laboratory searches for new isomers because many of these energetic forms possess unusual structures and rotational spectra that cannot be accurately estimated. At the present detection sensitivity, it may be possible to detect a number of other carbon chain molecules and their low-lying isomers if *ab initio* calculations are available as a guide.

Because it combines high sensitivity with high spectral resolution, Fourier transform microwave spectroscopy of supersonic molecular beams may be one of the best techniques to detect and characterize new isomers. The abundance of the long carbon chain HC₁₇N, for example, is estimated to be 3×10^6 HC₁₇N molecules/quantum state per gas pulse assuming that 10% of the molecules are in the beam waist of the Fabry–Perot cavity. Averaging over the large active volume of the cavity, the HC₁₇N concentration probably approaches 3000 molecules/quantum state/cm³ at 10 GHz—a low detection limit for almost any high-resolution technique, but an impressive one for microwave spectroscopy, which historically has not been particularly sensitive.

In addition to establishing the identity of a new molecule and providing precise spectroscopic constants for its ground state, the spectroscopy here provides another valuable piece of information: the specific abundance of a reactive molecule in the supersonic molecular beam. Assuming the dipole moment can be estimated or calculated, this abundance can be determined to an uncertainty of a factor of 3 or better—a sufficient level of accuracy to assess whether further studies in the infrared and visible (e.g., by laser-induced fluorescence or cavity ring-down spectroscopy) are then feasible.

TABLE III. Spectroscopic constants of bent HC₄N (in MHz).

Constant	Observed	Expected
<i>A</i>	31 983.967(1)	32 141 ^a
<i>B</i>	2 929.9161(4)	2 915 ^a
<i>C</i>	2 679.5644(5)	2 673 ^a
$\Delta_J \times 10^3$	1.614(2)	1.48 ^b
Δ_{JK}	−0.1417(1)	−0.140 ^b
$\delta_J \times 10^3$	0.402(8)	0.371 ^b
χ_{aa}	−3.279(2)	−3.05 ^c
$\chi_{bb} - \chi_{cc}$	−2.300(5)	−1.23 ^c
Δ^d	0.314 659(10)	0.33 ^b

^aThis work.

^bFrom analogous isomer of C₅H₂, see Ref. 20.

^cDerived on the assumption that the CN group is rotated by 26° with respect to the *a*-inertial axis.

^dThe inertial defect, $\Delta = I_C - I_A - I_B$.

Note added in proof. After submission of this article, we learned of the laboratory microwave detection of the linear triplet HC₄N isomer.²⁹

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