

Fourier transform microwave spectroscopy of vinylodiacetylene, vinyltriacetylene, and vinylcyanodiacetylene

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The rotational spectra of the three carbon chain molecules vinylodiacetylene (hex-1-ene-3,5-diyne, C₆H₄), vinyltriacetylene (oct-1-ene-3,5,7-triyne, C₈H₄), and its cyano analog vinylcyanodiacetylene (1-cyano-hex-5-ene-1,3-diyne, C₇H₃N) have been observed for the first time by Fourier transform microwave spectroscopy of a supersonic molecular beam. The molecules were observed as products of an electrical discharge through selected precursor mixtures: ethylene/diacetylene and vinylacetylene/diacetylene for the pure hydrocarbon molecules and vinylacetylene/cyanoacetylene for vinylcyanodiacetylene. The measurements yield precise sets of rotational constants that compare very well with theoretical constants obtained by quantum chemical calculations at the B3LYP/cc-pVTZ level of theory. Since these three carbon chains are similar in structure and composition to known astronomical molecules and because of their significant polarity, all three are candidates for radio astronomical detection. © 2005 American Institute of Physics. [DOI: 10.1063/1.1893920]

I. INTRODUCTION

Carbon chain molecules constitute the majority of the more than 130 molecules detected in interstellar clouds and circumstellar shells.¹ Of these, the cyanopolyynes H-(C≡C)_n-C≡N are especially prominent with those up to $n=5$ detected in the rich dark cloud source TMC-1.² As a result, cyanopolyynes have attracted much attention in the laboratory and chains up to $n=8$ have been detected by means of Fourier transform microwave (FTM) spectroscopy.³ Their pure hydrocarbon analogs, the polyacetylenes H-(C≡C)_n-H, lack a permanent electric dipole moment and therefore cannot be investigated by rotational spectroscopic techniques in the laboratory or observed with large radio telescopes in space. Despite this limitation, diacetylene, HC₄H, was detected for the first time in the infrared in Titan's atmosphere with a spectrometer aboard the Voyager spacecraft.⁴ Since then, diacetylene and longer polyacetylenes have eluded further astronomical detection until recently Cernicharo *et al.*⁵ reported on the detection of vibrational bands from diacetylene and triacetylene, HC₆H, in the protoplanetary nebula CRL 618 employing the Infrared Space Observatory, ISO. In the laboratory, polyacetylenes have been subjects of spectroscopic investigation for many years, mainly due to their importance as constituents of planetary atmospheres.⁶ Recently, Pino *et al.* reported the laboratory detection of polyacetylenes as heavy as HC₂₆H by ultraviolet spectroscopy.⁷

In contrast, spectroscopic data on partially hydrogenated forms of longer cyanopolyynes or polyacetylenes

(see Fig. 1)—all of which have fairly large dipole moments and are of significant astronomical interest—are sparse. Shorter members such as vinylacetylene (**8**) and vinyl cyanide (**2**)—dihydrogenated forms of diacetylene (**7**) and cyanoacetylene (**1**)—are well studied molecules in the laboratory,^{8,9} vinylcyanide (**2**) also being very prominent in space.¹⁰ A dihydrogenated form of triacetylene, hex-3-ene-1,5-diyne has been studied in the laboratory by microwave spectroscopy.¹¹ Moreover, three dihydrogenated forms of cyanodiacetylene, HC₅N, have been studied by means of microwave techniques: 1-cyano-but-3-ene-1-yne as well as the *cis/trans*-isomers of pent-2-en-4-yne nitrile.¹²⁻¹⁴ As far as we can tell, no spectroscopic data on other partially hydrogenated polyacetylenes and cyanopolyynes have been reported. All these molecules are plausible candidates for (radio) astronomical detection given the prominence of the unsaturated parent species in space. Astronomical detections of those molecules could provide important constraints on astrochemical models and improve our understanding of the formation of complex organic molecules in interstellar clouds and circumstellar shells. In the present investigation, compounds derived from formal dihydrogenation of the terminal ethynyl group in selected polyacetylenes or cyanopolyynes have been investigated in a molecular beam by means of Fourier transform microwave spectroscopy: vinylodiacetylene (**10**), vinyltriacetylene (**12**) (derived from triacetylene and tetraacetylene, respectively), and vinylcyanodiacetylene (**6**) 1-cyano-hex-5-ene-1,3-diyne, derived from HC₇N, see Fig. 1).

II. EXPERIMENTAL AND QUANTUM CHEMICAL CALCULATIONS

The FTM spectrometer used in the present investigation operates between 5 and 42 GHz and has been described in

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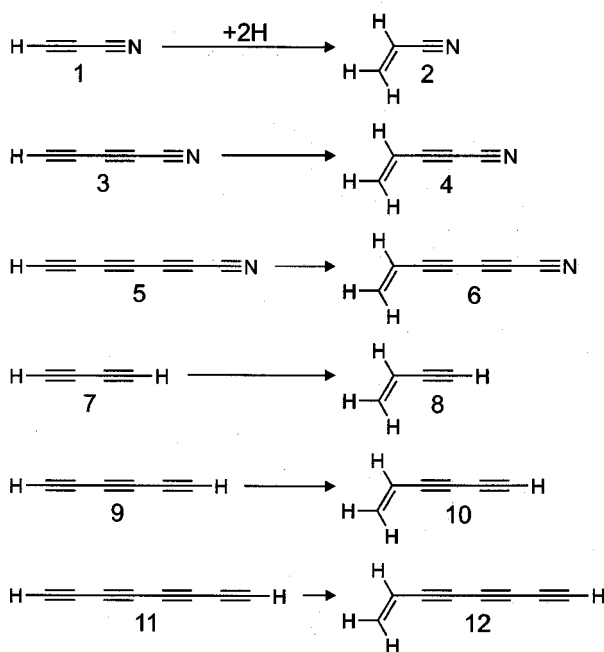


FIG. 1. Molecular structures of cyanoacetylenes and polyacetylenes and their vinyl derivatives obtained through formal dihydrogenation of the terminal ethynyl group.

detail elsewhere.¹⁵ Briefly, transient molecules are produced in a small electric discharge in the throat of a pulsed nozzle through a stream of organic precursor gases heavily diluted in a buffer gas (typically Ne). Free expansion from the pulsed nozzle into a large vacuum chamber forms a supersonic beam traveling at approximately Mach 2. Rotational transitions of molecules present in the beam are excited by a short pulse of resonant microwave radiation. The line emission from the coherently radiating molecules is then detected by a sensitive microwave receiver, and Fourier transformation of this free induction decay yields the power spectrum in the frequency domain, i.e., the line profile. In the present

experimental setup, each observed transition is split into two Doppler components since the molecular beam is parallel to the two traveling waves that compose the confocal mode of the Fabry–Perot cavity of the spectrometer.

The precursor gases in the present investigation (ethylene, C_2H_4 ; diacetylene, HC_4H ; vinylacetylene, $H_2C=CH-C\equiv C-H$; and cyanoacetylene, HC_3N) were subjected to the discharge in the presence of a large excess of Ne ($\sim 99\%$). The stagnation pressure behind the pulsed valve was typically 3.5 atm and the discharge potential was 1–1.3 kV.

The quantum chemical calculations of rotational constants and dipole moments reported here were done with the standard program package GAUSSIAN03 (Ref. 16) using the density functional theory (DFT) version B3LYP (Ref. 17) and Dunning's correlation consistent polarized valence basis set cc-pVTZ.¹⁸

III. RESULTS

A. Vinyl diacetylene, $H_2C=CH-(C\equiv C)_2-H$

Vinyl diacetylene (hex-1-ene-3,5-diyne, **10**) has been known to chemists for some 50 years,^{19,20} but surprisingly little is known about its spectral properties in the gas phase. Only a UV absorption spectrum²¹ and a resonant two-photon ionization spectrum²² have been reported to date. Very recently, a high-resolution electronic spectrum of the structurally similar $C_6H_4^+$ radical cation has been obtained.²³

In the present investigation, the pure rotational spectrum of vinyl diacetylene has been recorded for the first time by means of high-resolution FTM spectroscopy in a discharge through ethylene, C_2H_4 , and diacetylene, HC_4H . The spectroscopic search was guided by the *ab initio* rotational constants given in Table I. To tighten the frequency predictions, the theoretical constants A_e , B_e , and C_e were subjected to an empirical vibrational correction done as follows: scaling factors were obtained from a comparison of the experimentally derived rotational parameters of the structurally very closely

TABLE I. Molecular constants (in megahertz) of vinylcyanodiacetylene (**4**) and vinyl diacetylene (**10**).

Parameter	$H_2C=CH-C\equiv C-C\equiv N$ (4)			$H_2C=CH-(C\equiv C)_2-H$ (10)		
	Experimental ^a	<i>Ab initio</i> ^b	sf ^c	<i>Ab initio</i> ^b	sc ^d	Experimental ^e
A	39 922.(5)	41 404.2	0.964	42 005.8	40 493.6	40 490.(5)
B	1 376.633 51(9)	1 381.3	0.997	1 369.4	1 365.3	1 365.0813(1)
C	1 329.746 93(8)	1 336.7	0.995	1 326.1	1 319.5	1 319.5423(1)
$D_J \times 10^3$	0.106 3(2)					0.1010(2)
$D_{JK} \times 10^3$	-29.517(9)					-30.03(2)
$d_1 \times 10^6$	-15.3(2)					-14.6(2)
rms						0.0012
wrms ^f						0.58
μ_a ^g						0.76
μ_b ^g						0.04

^aReference 12.

^bB3LYP/cc-pVTZ.

^cScaling factors, see text.

^dScaled constants.

^eThis work.

^fWeighted rms (dimensionless).

^gIn debye (B3LYP/cc-pVTZ).

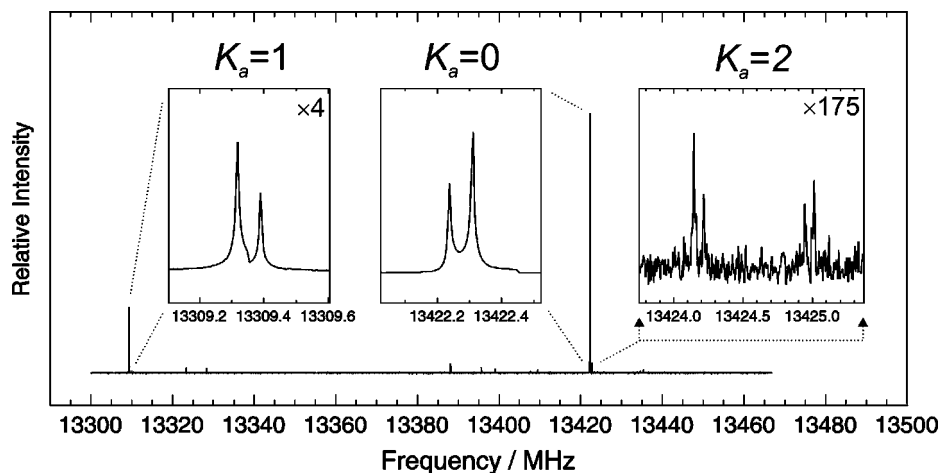


FIG. 2. Microwave spectrum of vinylacetylene showing the lower $K_a=1$ component, the $K_a=0$ component, and the $K_a=2$ asymmetry doublet of the $J=5-4$ rotational transition at 13.4 GHz. The spectrum is a composite of single spectra recorded with a step size of 400 kHz. 250 cycles were averaged at each setting of the Fabry-Perot cavity. The repetition rate was 6 Hz and the length and polarization power of the microwave pulses applied were 1 μ s and ~ 1 mW, respectively.

related compound vinylcyanoacetylene (1-cyanobut-3-ene-1-yne, **4**) (Ref. 12) and the corresponding theoretically calculated molecular parameters (Table I). Scaled rotational constants for vinylacetylene were obtained by multiplying these correction factors with the equilibrium parameters obtained from theory. Based on these empirically derived ground state rotational constants, vinylacetylene was readily identified in a search at 13.4 GHz for the $J=5-4$ transition, which yielded the spectra shown in Fig. 2.

In total, 50 a -type transitions were measured in the frequency range 8–40 GHz covering the rotational quantum numbers $2 \leq J \leq 15$ and $0 \leq K_a \leq 2$. The data are summarized in Table II. Line fitting was done with Pickett's program SPFIT (Ref. 24) employing a Watson Hamiltonian in the S reduction²⁵ yielding the set of molecular parameters given in Table I. As can be seen, the empirical vibrational correction worked out very well: The calculated (equilibrium) rotational constants for the isovalent vinylcyanoacetylene (**4**) match the

TABLE II. Experimental rotational transition frequencies of vinylacetylene (in megahertz) and residuals $o-c$ (in kilohertz).

$J'_{K'_a K'_c} - J''_{K''_a K''_c}$	Frequency ^a	$o-c$	$J'_{K'_a K'_c} - J''_{K''_a K''_c}$	Frequency ^a	$o-c$
3 _{1,3} -2 _{1,2}	7 985.7076	-0.7	8 _{2,7} -7 _{2,6}	21 478.2207	2.2
3 _{0,3} -2 _{0,2}	8 053.7004	-0.6	8 _{2,6} -7 _{2,5}	21 481.5537	-0.8
3 _{1,2} -2 _{1,1}	8 122.3223	0.1	8 _{1,7} -7 _{1,6}	21 658.5908	-0.8
4 _{1,4} -3 _{1,3}	10 647.5552	0.1	9 _{1,9} -8 _{1,8}	23 955.8320	-1.5
4 _{0,4} -3 _{0,3}	10 738.0698	-1.5	9 _{0,9} -8 _{0,8}	24 156.5527	0.0
4 _{2,3} -3 _{2,2}	10 739.4004	1.8	9 _{2,8} -8 _{2,7}	24 162.7656	0.4
4 _{2,2} -3 _{2,1}	10 739.7949	-1.0	9 _{2,7} -8 _{2,6}	24 167.5293	-1.1
4 _{1,3} -3 _{1,2}	10 829.7041	0.5	9 _{1,8} -8 _{1,7}	24 365.5898	0.1
5 _{1,5} -4 _{1,4}	13 309.3540	0.0	10 _{1,10} -9 _{1,9}	26 617.2173	1.4
5 _{0,5} -4 _{0,4}	13 422.2730	0.0	10 _{0,10} -9 _{0,9}	26 839.2813	0.4
5 _{2,4} -4 _{2,3}	13 424.1816	1.1	10 _{2,9} -9 _{2,8}	26 847.2324	1.7
5 _{2,3} -4 _{2,2}	13 424.9717	-3.3	10 _{1,9} -9 _{1,8}	27 072.4729	0.5
5 _{1,4} -4 _{1,3}	13 537.0347	0.7	11 _{1,11} -10 _{1,10}	29 278.4795	-0.6
6 _{1,6} -5 _{1,5}	15 971.0942	1.1	11 _{0,11} -10 _{0,10}	29 521.5879	-0.8
6 _{0,6} -5 _{0,5}	16 106.2647	0.7	11 _{1,10} -10 _{1,9}	29 779.2271	0.8
6 _{2,5} -5 _{2,4}	16 108.9180	0.9	12 _{1,12} -11 _{1,11}	31 939.6162	1.5
6 _{2,4} -5 _{2,3}	16 110.3057	-1.7	12 _{0,12} -11 _{0,11}	32 203.4356	1.0
6 _{1,5} -5 _{1,4}	16 244.3018	1.1	12 _{1,11} -11 _{1,10}	32 485.8369	-1.5
7 _{1,7} -6 _{1,6}	18 632.7598	-0.7	13 _{1,13} -12 _{1,12}	34 600.6074	-1.3
7 _{0,7} -6 _{0,6}	18 790.0020	-0.3	13 _{0,13} -12 _{0,12}	34 884.7754	-1.6
7 _{2,6} -6 _{2,5}	18 793.5987	-0.7	13 _{1,12} -12 _{1,11}	35 192.2949	-0.2
7 _{2,5} -6 _{2,4}	18 795.8223	-1.4	14 _{1,14} -13 _{1,13}	37 261.4532	2.4
7 _{1,6} -6 _{1,5}	18 951.4903	-0.6	14 _{0,14} -13 _{0,13}	37 565.5743	-0.5
8 _{1,8} -7 _{1,7}	21 294.3448	0.3	14 _{1,13} -13 _{1,12}	37 898.5840	1.0
8 _{0,8} -7 _{0,7}	21 473.4473	1.4	15 _{1,15} -14 _{1,14}	39 922.1289	-1.3

^aEstimated experimental uncertainties (1σ) are 2 kHz.

TABLE III. Molecular constants (in megahertz) of vinylcyanodiacetylene (**6**) and vinyltriacetylene (**12**).

Parameter	H ₂ C=CH-(C≡C) ₂ -C≡N			H ₂ C=CH-(C≡C) ₃ -H		
	Experimental	<i>Ab initio</i> ^a	sf ^b	<i>Ab initio</i> ^a	sc ^c	Experimental
<i>A</i>	36 061.(41)	37 280.4	0.967	37 736.5	36 491.2	36 352.(90)
<i>B</i>	569.198 74(5)	572.2	0.995	573.4	570.5	570.6039(1)
<i>C</i>	560.089 14(5)	563.5	0.994	564.9	561.5	561.5390(1)
<i>D_J</i> × 10 ⁶	11.65(6)					11.3(2)
<i>D_{JK}</i> × 10 ³	-14.57(4)					-14.62(7)
<i>d₁</i> × 10 ⁶	-1.32(4)					-1.4(1)
<i>χ_{aa}</i>	-4.2(1)					
<i>χ_{bb}</i>	2.1(2)					
rms	0.0012					0.0008
wrms ^d	0.58					0.40
<i>μ_a</i> ^e	6.12					1.05
<i>μ_b</i> ^e	0.15					0.08

^aB3LYP/cc-pVTZ.^bScaling factors, see text.^cScaled constants.^dWeighted rms (dimensionless).^eIn debye (B3LYP/cc-pVTZ).

ground vibrational state constants obtained by FTM spectroscopy¹² to within 1%. Employing the empirical vibrational correction on vinyltriacetylene (**10**) yields a value for the scaled rotational constant $(B+C)/2$ of 1342.4 MHz differing by only 100 kHz or 0.01% from the experimental value of 1342.3 MHz. The weighted rms of 0.5 shows that the data are reproduced to within the estimated experimental errors of 2 kHz. The quartic centrifugal distortion constants D_J , D_{JK} , and d_1 also agree very well for both molecules, owing to the close structural similarity of the two.

B. Vinylcyanodiacetylene, H₂C=CH-(C≡C)₂-C≡N, and vinyltriacetylene, H₂C=CH-(C≡C)₃-H

Vinylcyanodiacetylene (1-cyanohept-5-ene-1,3-diyne, hept-6-ene-2,4-diyne, **6**) has to our knowledge not

been previously reported. In a search guided by the *ab initio* rotational constants in Table III, the molecule was detected in a discharge through a mixture of vinylacetylene and cyanoacetylene. A sample survey spectrum showing the initial detection of vinylcyanodiacetylene via its $J=7_{0,7}-6_{0,6}$ rotational transition is shown in Fig. 3 where the nitrogen hyperfine structure is clearly resolved. Table IV summarizes the data for the 42 measured rotational transitions and Table III gives the fitted spectroscopic constants. The derived $(B+C)/2$ of 564.6 MHz agrees with the theoretical equilibrium value of 567.9 MHz to better than 1%. Most of the lines of vinylcyanodiacetylene show distinct nitrogen hyperfine structure yielding the nuclear quadrupole coupling constants χ_{aa} and χ_{bb} in Table III. These values are very close to those of the shorter chain vinylcyanoacetylene.¹² The difference of

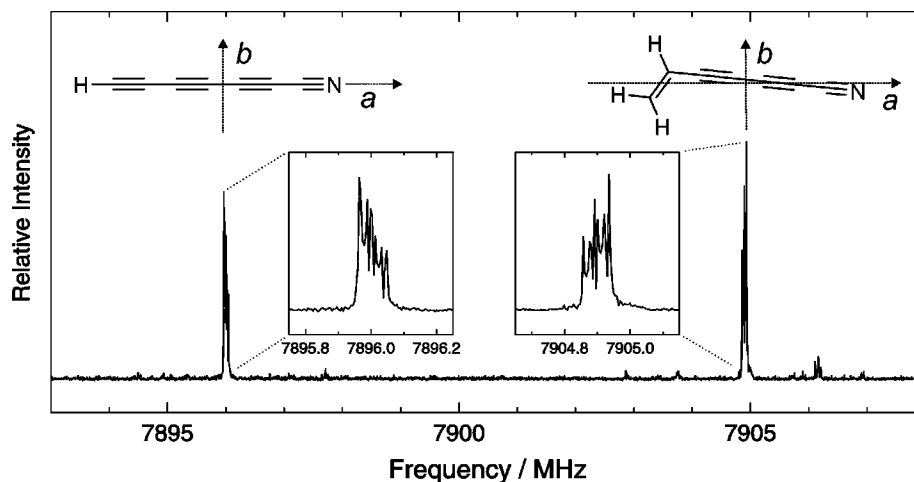


FIG. 3. First laboratory detection of vinylcyanodiacetylene showing the $J=7_{0,7}-6_{0,6}$ rotational transition at 7905 MHz. This transition is closely accompanied by the corresponding transition $J=7-6$ of cyanotriacetylene, HC₇N, at 7896 MHz, a molecule also being produced in the discharge. The figure also shows the molecular structures and their orientations in the *ab* main inertial plane. Despite the greater mass of the vinyl compound, the small rotation about the *c* main inertial axis (which stands perpendicular on the *ab* plane) is sufficient to lower the moment of inertia about the *b* axis compared to HC₇N, and leads to a slightly larger effective $\bar{B}=(B+C)/2$ in vinylcyanodiacetylene (see text). In addition to Doppler doubling, nitrogen hyperfine structure is clearly present. The experimental conditions to obtain this spectrum were the same as those in Fig. 2 except that the polarization power was $\sim 10 \mu\text{W}$.

TABLE IV. Experimental rotational transition frequencies of vinylcyanodiacetylene (in megahertz) and residuals *o-c* (kilohertz).

$J'_{K'_a, K'_c} - J''_{K''_a, K''_c}$	$F' - F''$	Frequency ^a	<i>o-c</i>	$J'_{K'_a, K'_c} - J''_{K''_a, K''_c}$	$F' - F''$	Frequency ^a	<i>o-c</i>
6 _{0,6} -5 _{0,5}	5-4	6 775.6248	0.7	12 _{1,11} -11 _{1,10}	11-10	13 606.2446	-0.5
6 _{0,6} -5 _{0,5}	6-5	6 775.6545	-1.3	12 _{1,11} -11 _{1,10}	12-11	13 606.2446	-0.5
6 _{0,6} -5 _{0,5}	7-6	6 775.6724	0.4	12 _{1,11} -11 _{1,10}	13-12	13 606.2569	1.7
7 _{1,7} -6 _{1,6}	7-6	7 873.2786	-1.0	13 _{1,13} -12 _{1,12}	12-11	14 621.6573	-1.0
7 _{1,7} -6 _{1,6}	6-5	7 873.2898	0.6	13 _{1,13} -12 _{1,12}	13-12	14 621.6573	-1.0
7 _{1,7} -6 _{1,6}	8-7	7 873.3165	-1.1	13 _{1,13} -12 _{1,12}	14-13	14 621.6685	1.6
7 _{0,7} -6 _{0,6}	6-5	7 904.8794	0.4	13 _{0,13} -12 _{0,12}	12-11	14 679.9947	-1.9
7 _{0,7} -6 _{0,6}	7-6	7 904.8997	-1.3	13 _{0,13} -12 _{0,12}	13-12	14 680.0020	0.0
7 _{0,7} -6 _{0,6}	8-7	7 904.9121	-1.2	13 _{0,13} -12 _{0,12}	14-13	14 680.0074	1.3
7 _{1,6} -6 _{1,5}	7-6	7 937.0425	-0.6	13 _{1,12} -12 _{1,11}	12-11	14 740.0581	-1.1
7 _{1,6} -6 _{1,5}	6-5	7 937.0545	1.4	13 _{1,12} -12 _{1,11}	13-12	14 740.0581	-1.1
7 _{1,6} -6 _{1,5}	8-7	7 937.0794	-1.5	13 _{1,12} -12 _{1,11}	14-13	14 740.0708	3.1
8 _{1,8} -7 _{1,7}	8-7	8 998.0283	-0.7	14 _{0,14} -13 _{0,13}	13-12	15 809.0987	-1.6
8 _{1,8} -7 _{1,7}	7-6	8 998.0347	1.1	14 _{0,14} -13 _{0,13}	14-13	15 809.1084	1.6
8 _{1,8} -7 _{1,7}	9-8	8 998.0552	-0.9	14 _{0,14} -13 _{0,13}	15-14	15 809.1084	1.6
8 _{0,8} -7 _{0,7}	7-6	9 034.1162	0.4	14 _{1,13} -13 _{1,12}	13-12	15 873.8624	-0.9
8 _{0,8} -7 _{0,7}	8-7	9 034.1304	-1.5	14 _{1,13} -13 _{1,12}	14-13	15 873.8624	-0.9
8 _{0,8} -7 _{0,7}	9-8	9 034.1421	0.5	14 _{1,13} -13 _{1,12}	15-14	15 873.8711	0.6
8 _{1,7} -7 _{1,6}	8-7	9 070.8999	-0.4	15 _{0,15} -14 _{0,14}	14-13	16 938.1758	0.3
8 _{1,7} -7 _{1,6}	7-6	9 070.9058	0.7	15 _{0,15} -14 _{0,14}	15-14	16 938.1826	1.5
8 _{1,7} -7 _{1,6}	9-8	9 070.9277	0.5	15 _{0,15} -14 _{0,14}	16-15	16 938.1826	1.5
9 _{1,9} -8 _{1,8}	9-8	10 122.7725	1.1	15 _{1,14} -14 _{1,13}	14-13	17 007.6563	-0.5
9 _{1,9} -8 _{1,8}	8-7	10 122.7725	1.1	15 _{1,14} -14 _{1,13}	15-14	17 007.6563	-0.5
9 _{1,9} -8 _{1,8}	10-9	10 122.7901	-0.5	15 _{1,14} -14 _{1,13}	16-15	17 007.6651	2.1
9 _{0,9} -8 _{0,8}	8-7	10 163.3350	0.8	16 _{1,16} -15 _{1,15}	15-14	17 995.7305	-0.1
9 _{0,9} -8 _{0,8}	9-8	10 163.3448	-1.8	16 _{1,16} -15 _{1,15}	16-15	17 995.7305	-0.1
9 _{0,9} -8 _{0,8}	10-9	10 163.3545	0.1	16 _{1,16} -15 _{1,15}	17-16	17 995.7373	1.2
9 _{1,8} -8 _{1,7}	9-8	10 204.7490	-1.0	16 _{0,16} -15 _{0,15}	15-14	18 067.2237	0.2
9 _{1,8} -8 _{1,7}	8-7	10 204.7490	-1.0	16 _{0,16} -15 _{0,15}	16-15	18 067.2237	0.2
9 _{1,8} -8 _{1,7}	10-9	10 204.7666	-2.4	16 _{0,16} -15 _{0,15}	17-16	18 067.2237	0.2
10 _{1,10} -9 _{1,9}	10-9	11 247.5049	0.2	17 _{1,17} -16 _{1,16}	16-15	19 120.3994	-0.9
10 _{1,10} -9 _{1,9}	9-8	11 247.5049	0.2	17 _{1,17} -16 _{1,16}	17-16	19 120.3994	-0.9
10 _{1,10} -9 _{1,9}	11-10	11 247.5186	-1.3	17 _{1,17} -16 _{1,16}	18-17	19 120.4053	0.2
10 _{0,10} -9 _{0,9}	9-8	11 292.5352	2.0	17 _{0,17} -16 _{0,16}	16-15	19 196.2354	0.3
10 _{0,10} -9 _{0,9}	10-9	11 292.5415	-1.4	17 _{0,17} -16 _{0,16}	17-16	19 196.2354	0.3
10 _{0,10} -9 _{0,9}	11-10	11 292.5503	0.9	17 _{0,17} -16 _{0,16}	18-17	19 196.2354	0.3
10 _{1,9} -9 _{1,8}	10-9	11 338.5899	-0.0	17 _{1,16} -16 _{1,15}	16-15	19 275.2080	-0.9
10 _{1,9} -9 _{1,8}	9-8	11 338.5899	-0.0	17 _{1,16} -16 _{1,15}	17-16	19 275.2080	-0.9
10 _{1,9} -9 _{1,8}	11-10	11 338.6036	-1.4	17 _{1,16} -16 _{1,15}	18-17	19 275.2149	1.2
11 _{1,11} -10 _{1,10}	11-10	12 372.2305	-0.1	18 _{1,18} -17 _{1,17}	^b	20 245.0586	-1.3
11 _{1,11} -10 _{1,10}	10-9	12 372.2305	-0.1	18 _{0,18} -17 _{0,17}	^b	20 325.2129	0.6
11 _{1,11} -10 _{1,10}	12-11	12 372.2437	0.8	18 _{1,17} -17 _{1,16}	^b	20 408.9668	-0.8
11 _{0,11} -10 _{0,10}	10-9	12 421.7090	-2.1	19 _{0,19} -18 _{0,18}	^b	21 454.1543	1.4
11 _{0,11} -10 _{0,10}	11-10	12 421.7183	-0.7	20 _{0,20} -19 _{0,19}	^b	22 583.0557	0.6
11 _{0,11} -10 _{0,10}	12-11	12 421.7266	2.1	21 _{1,21} -20 _{1,20}	^b	23 618.9590	1.5
11 _{1,10} -10 _{1,9}	10-9	12 472.4219	0.1	21 _{0,21} -20 _{0,20}	^b	23 711.9160	-0.8
11 _{1,10} -10 _{1,9}	11-10	12 472.4219	0.1	21 _{1,20} -20 _{1,19}	^b	23 810.1524	-1.4
11 _{1,10} -10 _{1,9}	12-11	12 472.4346	0.6	22 _{1,22} -21 _{1,21}	^b	24 743.5616	-0.9
12 _{1,12} -11 _{1,11}	11-10	13 496.9478	-0.9	22 _{0,22} -21 _{0,21}	^b	24 840.7344	-1.5
12 _{1,12} -11 _{1,11}	12-11	13 496.9478	-0.9	22 _{1,21} -21 _{1,20}	^b	24 943.8526	0.8
12 _{1,12} -11 _{1,11}	13-12	13 496.9605	1.6				
12 _{0,12} -11 _{0,11}	11-10	13 550.8647	-1.5				
12 _{0,12} -11 _{0,11}	12-11	13 550.8726	-0.1				
12 _{0,12} -11 _{0,11}	13-12	13 550.8784	1.0				

^aEstimated experimental uncertainties (1σ) are 2 kHz.^bHyperfine structure not resolved.

TABLE V. Experimental rotational transition frequencies of vinyltriacetylene (in megahertz) and residuals *o-c* (kilohertz).

$J'_{K'_a K'_c} - J''_{K''_a K''_c}$	Frequency ^a	<i>o-c</i>	$J'_{K'_a K'_c} - J''_{K''_a K''_c}$	Frequency ^a	<i>o-c</i>
6 _{1,6} -5 _{1,5}	6 765.8169	0.7	13 _{1,13} -12 _{1,12}	14 659.0767	0.9
6 _{0,6} -5 _{0,5}	6 792.7876	-0.2	13 _{0,13} -12 _{0,12}	14 717.1319	-0.6
6 _{1,5} -5 _{1,4}	6 820.2029	-0.3	13 _{1,12} -12 _{1,11}	14 776.8941	-0.5
7 _{1,7} -6 _{1,6}	7 893.4419	-0.2	14 _{1,14} -13 _{1,13}	15 786.6548	-0.2
7 _{0,7} -6 _{0,6}	7 924.8899	1.0	14 _{0,14} -13 _{0,13}	15 849.0942	0.1
7 _{1,6} -6 _{1,5}	7 956.8928	0.2	14 _{1,13} -13 _{1,12}	15 913.5318	-0.6
8 _{1,8} -7 _{1,7}	9 021.0630	-0.3	15 _{1,15} -14 _{1,14}	16 914.2246	-0.3
8 _{0,8} -7 _{0,7}	9 056.9761	0.1	15 _{0,15} -14 _{0,14}	16 981.0283	0.5
8 _{1,7} -7 _{1,6}	9 093.5767	-0.1	15 _{1,14} -14 _{1,13}	17 050.1611	1.3
9 _{1,9} -8 _{1,8}	10 148.6807	1.6	16 _{1,16} -15 _{1,15}	18 041.7862	1.4
9 _{0,9} -8 _{0,8}	10 189.0479	0.8	16 _{0,16} -15 _{0,15}	18 112.9317	0.0
9 _{1,8} -8 _{1,7}	10 230.2559	0.8	16 _{1,15} -15 _{1,14}	18 186.7754	-0.7
10 _{1,10} -9 _{1,9}	11 276.2859	-3.1	17 _{1,17} -16 _{1,16}	19 169.3330	-1.1
10 _{0,10} -9 _{0,9}	11 321.0996	-0.8	17 _{0,17} -16 _{0,16}	19 244.8037	0.0
10 _{1,9} -9 _{1,8}	11 366.9268	0.0	17 _{1,16} -16 _{1,15}	19 323.3809	0.3
11 _{1,11} -10 _{1,10}	12 403.8921	-0.1	18 _{0,18} -17 _{0,17}	20 376.6416	-0.3
11 _{0,11} -10 _{0,10}	12 453.1338	0.1	19 _{0,19} -18 _{0,18}	21 508.4434	-0.9
11 _{1,10} -10 _{1,9}	12 503.5909	-0.2	20 _{0,20} -19 _{0,19}	22 640.2100	1.1
12 _{1,12} -11 _{1,11}	13 531.4888	0.8	21 _{0,21} -20 _{0,20}	23 771.9336	-0.2
12 _{0,12} -11 _{0,11}	13 585.1446	-0.5			
12 _{1,11} -11 _{1,10}	13 640.2471	-0.2			

^aEstimated experimental uncertainties (1σ) are 2 KHz.

($B+C$)/2 of vinylcyanodiacetylene and B of linear HC₇N is only 600 kHz (564.6 vs 564.0 MHz) which explains why the $J=7_{0,7}$ -6_{0,6} and $J=7$ -6 transitions can be found together in the narrow survey scan shown in Fig. 3.

The hydrocarbon vinyltriacetylene has apparently not been previously studied. Recently, a cavity ring-down optical detection of the related radical cation C₈H₄⁺ was reported,²⁶ but rotational structure was not resolved. Once the experimental set of molecular parameters of vinylcyanodiacetylene were in hand, the same empirical scaling technique as for the vinylcyanoacetylene/vinyldiacetylene pair was applied to the calculated rotational constants of vinyltriacetylene (Table III). On the basis of these scaled predictions, the molecule was found readily in a discharge of vinylacetylene and diacetylene. Forty lines covering $5 \leq J \leq 21$ and $K_a=0, 1$ were recorded which are collected in Table V. The derived molecular constants are shown in Table III in comparison to the cyano analog vinylcyanodiacetylene. Owing to the structural relationship of both molecules their rotational constants are very similar. Within the experimental uncertainties, the values obtained for the quartic centrifugal distortion coefficients are practically identical.

IV. DISCUSSION

All three vinyl carbon chain molecules presented here have been observed by their *a*-type pure rotational spectra exclusively. Owing to the large A rotational constants of at least 36 GHz, the frequencies $\nu=A+C$ of the fundamental *b*-type transitions 1_{1,1}-0_{0,0} fall in a frequency range of our FTM spectrometer which has poor sensitivity. In addition,

the *b*-type dipole moment components μ_b are calculated to be very small for all three molecules, of order 0.15 D for vinylcyanodiacetylene and <0.1 D for the two pure hydrocarbons. The magnitudes of the *a*-type dipole moment components calculated here are substantial in all three cases (see Tables I and III). The values obtained for the vinylacetylenes are $\mu_a=0.76$ D and 1.05 D for vinyldiacetylene and vinyltriacetylene, respectively. As expected, the corresponding value for vinylcyanodiacetylene is significantly larger, $\mu_a=6.12$ D. A recent study of somewhat smaller related carbon chain molecules suggests that these values should be accurate to of order 10%.¹² A comparison between a DFT calculation for HC₇N performed at the B3LYP/cc-pVTZ level and a more sophisticated and accurate coupled-cluster calculation by Botschwina and co-workers²⁷ (5.24 vs 4.89) D suggests that the values obtained in the present investigation may be slightly overestimated but are still fairly reliable.

Many other molecules, some similar to those investigated here, probably exist in our molecular beam. In the present investigation, discharging a vinylcyanide/acetylene mixture was found to be a source of *cis*- (**13**) and *trans*-pent-2-ene-4-yne nitrile (**14**, Fig. 4). Accordingly, the branched nitrile **15** (2-cyano-but-1-ene-3-yne) should also be accessible via the same route, a molecule apparently not yet described in the chemical literature.

Following the gas-phase investigations of *o*-benzynes (Ref. 28 and references therein) and hex-3-ene-1,5-diyne (Ref. 11) by FTM spectroscopy, the present study of vinyldiacetylene marks the third characterization of a C₆H₄ isomer by high-resolution spectroscopic techniques. In analogy to the route proposed for nitrile **15**, by replacing vinyl cyanide with vinylacetylene, the branched C₆H₄ isomer

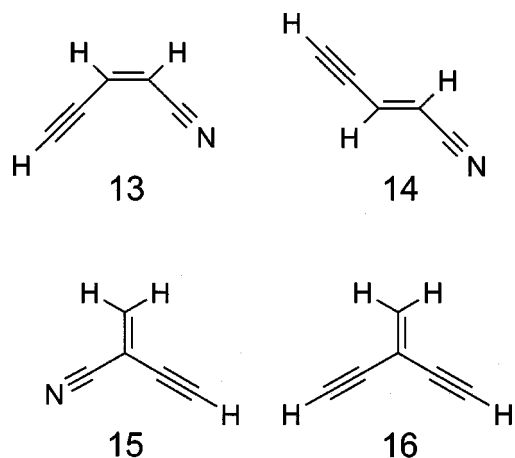


FIG. 4. Molecular structures of *cis*-pent-2-ene-4-yne-1-nitrile (**13**), *trans*-pent-2-ene-4-yne-1-nitrile (**14**), 2-cyano-but-1-ene-3-yne (**15**) and its pure hydrocarbon analog 3-methylenepent-1,4-diyne (**16**).

3-methylenepent-1,4-diyne (**16**) may be accessible, a molecule for which no high-resolution spectroscopic data is yet available (cf. Ref. 21).

The data obtained here allow for subsequent radio astronomical searches with the presently most powerful radio telescopes such as the MPIFR 100 m, the Green Bank 100 m or the IRAM 30 m telescopes. The simplest vinyl cyano compound, vinyl cyanide, $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$, has been detected in many different astronomical environments.¹⁰ The next member in the series, vinylcyanoacetylene $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, has been searched for unsuccessfully.²⁹ No pure hydrocarbon vinyl compound has yet been detected, but astrochemical modeling suggests that vinylacetylene, $\text{H}_2\text{C}=\text{CH}-\text{C}=\text{CH}$, is a likely molecular constituent of proto-planetary nebulae, where it is plausibly formed in a neutral-neutral reaction between C_2H_4 and C_2H .³⁰ Vinylacetylenes are also thought to play roles in carbon condensation processes as well as the formation of polycyclic aromatic hydrocarbons in space.³¹ Given the wide distribution of its cyano analogue vinyl cyanide in space, vinylacetylene may also be present in other astronomical sources such as hot cores. Its rotational spectrum is well known from previous laboratory studies⁸ and with the data presented here radio astronomical searches can now also be undertaken for the longer relatives vinylodiacetylene and vinyltriacetylene as well as for the cyano analog of the latter, vinylcyanodiacetylene.

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- ¹See the Cologne Database for Molecular Spectroscopy at <http://www.cdms.de> for an up-to-date summary of astronomically detected molecules. The database has been described in detail by H. S. P. Müller, S. Thorwirth, D. A. Roth, and G. Winnewisser, *Astron. Astrophys.* **370**, L49 (2001).
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