and $Fe^{III}Fe^{III}$ forms of MMOH, based on their Mössbauer-determined percentages in the freeze-quenched samples. For sample 1, the pre-edge area of Q = {22 units − [(27%)(10 units)] − [(12%)(14 units)]}/61% = 29 units. For sample 2, the pre-edge area of Q = {18 units − [(33%)(10 units)] − [(23%)(14 units)]}/44% = 26 units.
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Detection and Characterization of the Cumulene Carbenes H_2C_5 and H_2C_6

M. C. McCarthy,* M. J. Travers, A. Kovács, Wei Chen,
Stewart E. Novick, C. A. Gottlieb, P. Thaddeus

Two cumulene carbenes, H_2C_5 and H_2C_6, were detected in a supersonic molecular beam by Fourier transform microwave spectroscopy. Their rotational and leading centrifugal distortion constants were determined with high accuracy, such that the entire radio spectrum can now be calculated. Like the known carbenes H_2C_3 and H_2C_4, both molecules have singlet electronic ground states and linear carbon-chain backbones. They can be produced in sufficiently high concentrations in the laboratory that their electronic spectra, expected to lie in the visible, should be readily detectable by laser spectroscopy. The microwave spectra of other, more exotic isomers may be detectable as well.

Carbenes are highly reactive organic molecules with two nonbonded electrons localized on a single C atom. They are important intermediates in terrestrial chemistry, and several have now been detected in the interstellar gas or in circumstellar shells (*1*). Of particular interest in both combustion processes and astrochemistry are the cumulene carbene chains $H_2C{=}(C{=})_nC{:}$, which may be important building blocks in the syntheses of long hydrocarbons and pure C chains implicated in the formation of fullerenes (*2*). Like organic dyes, cumulene carbenes are likely to have intense optical electronic transitions, which may provide a powerful and convenient way to monitor combustion processes, and they are promising candidates for carriers of the interstellar optical diffuse bands, the identification of which constitutes one of the outstanding unsolved problems in astronomical spectroscopy (*3*). Gas phase studies that establish the geometric and electronic structure of such C chain carbenes are essential if we are to understand their chemical reactivities (*4*), but few have been studied spectroscopically because of their high reactivity. Although we have recently detected long hydrocarbon radicals and closed shell cyanopolyynes (for example, $C_{11}H$ and $HC_{13}N$), the longest cumulene carbene known to date is H_2CCCC (*5*).

By using Fourier transform microwave (FTM) spectroscopy (*6*) of a supersonic molecular beam (Fig. 1), we have now detected the next two members of the cumulene carbene sequence, H_2C_5 ($H_2C{=}C{=}C{=}C{=}C{:}$, pentatetraenylidene) and H_2C_6 ($H_2C{=}C{=}C{=}C{=}C{=}C{:}$, hexapentaenylidene). Nine *a*-type *R*-branch ($\Delta J = 1$, where J is the rotational angular momentum quantum number) transitions of H_2C_5 and 13 transitions of H_2C_6 were measured in the frequency range from 8 to 23 GHz. In both molecules, the rotational transitions are grouped into fairly tight triplets with an intensity ratio of approximately 3:2:3 and a splitting of about ±0.1% of the frequency (for example, ±17 MHz at 13.4 GHz for H_2C_6). The relative intensities are those expected at low temperature for a slightly asymmetric top with two equivalent H atoms, and the splitting is in quantitative agreement with that calculated by scaling from the rotational constants of H_2C_3 (*7*) and H_2C_4 (*5*). Because of ortho-para spin statistics, rotational levels where K (the projection of the rotational angular momentum on the C_2 symmetry axis) is ± 1, which lie about 14 K above the $K = 0$ levels in both carbenes (Fig. 2), are metastable. Therefore, they are populated in our molecular beam even though the rotational temperature is only about 3 K.

We determined spectroscopic constants by fitting a theoretical spectrum calculated from a standard asymmetric top Hamiltonian (*8*) to the observed frequencies. Two rotational constants (B and C) and two centrifugal distortion constants (D_J and D_{JK}) were obtained for each carbene (Table 1). Transition frequencies ($\nu_{J \leftarrow J-1}$) for the $K = 0$ and the two $K = \pm 1$ ladders of each can be calculated from the approximate expression

Table 1. Spectroscopic constants of H_2C_5 and H_2C_6 (in megahertz). These rotational and centrifugal distortion constants are from a least squares fit of Watson's *S*-reduced Hamiltonian. The root mean square (3 kHz) of the fits is comparable to the measurement uncertainties. Uncertainties (1σ) are in units of the last significant digit.

Constant	H_2C_5 Laboratory	H_2C_5 Expected*	H_2C_6 Laboratory	H_2C_6 Expected*
A	277,600†	287,600	268,400†	286,100
B	2,304.7844(3)	2,304(5)	1,348.0891(1)	1,345(2)
C	2,285.8053(3)	2,285(5)	1,341.3519(1)	1,341(2)
$D_J \times 10^3$	0.104(6)	0.088‡	0.0283(12)	0.0353§
D_{JK}	0.0464(2)		0.0164(1)	

*From (*10*). †Derived assuming a planar structure, that is, $1/C - 1/A - 1/B = 0$. ‡From (*27*). §From (*28*).

M. C. McCarthy, M. J. Travers, P. Thaddeus, Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA, and Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA.
A. Kovács and C. A. Gottlieb, Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA.
W. Chen and S. E. Novick, Department of Chemistry, Wesleyan University, Middletown, CT 06459, USA.

*To whom correspondence should be addressed.

$$\nu_{J\leftarrow J-1} = \left[(B + C) \pm \frac{1}{2}(B - C)\delta_{K,1} - 2D_{JK}K^2\right]J - \left\{4D_J + \frac{(B - C)^2}{c[A - (B + C)/2]}\right\}J^3 \quad (1)$$

where $\delta_{K,1}$ is a Kronecker delta and c (a numerical constant) is 32 for $K = \pm 1$ and 8 for $K = 0$. This expression contains only the leading terms in the power series expansion of Polo (*9*). The frequencies agree with those calculated from the truncated asymmetric top Hamiltonian to within 0.4 km s^{-1} up to 300 GHz; at that frequency, neglect of the higher order centrifugal distortion terms in the Hamiltonian introduces an uncertainty of ≤1 km s^{-1}. The rotational constants of H_2C_5 and H_2C_6 are within 0.25% of those calculated from ab initio equilibrium geometries of Maluendes and McLean (*10*) and high-level (coupled cluster theory) equilibrium geometries of Botschwina (*11*). The distortion constants D_J are in good agreement with those of other species with similar structure and size. Further evidence for the identifications of the molecules was obtained in a deuterium-enriched discharge, where the rotational spectra of D_2C_5 (Fig. 3) and D_2C_6 were observed. Their rotational constants are those predicted by scaling from the normal species, and the components of the rotational triplets now have an intensity ratio of 1:4:1, as expected for a molecule having two equivalent bosons, each of spin 1 (*12*).

Both cumulene carbenes were observed in singlet electronic states, the same spin multiplicity as found for the shorter chains H_2C_3 (*7*) and H_2C_4 (*5*). The rotational spectra of H_2C_5 and H_2C_6 are consistent with linear C backbones, and, although small departures from linearity are difficult to detect spectroscopically, in the present case such departures must be small. The

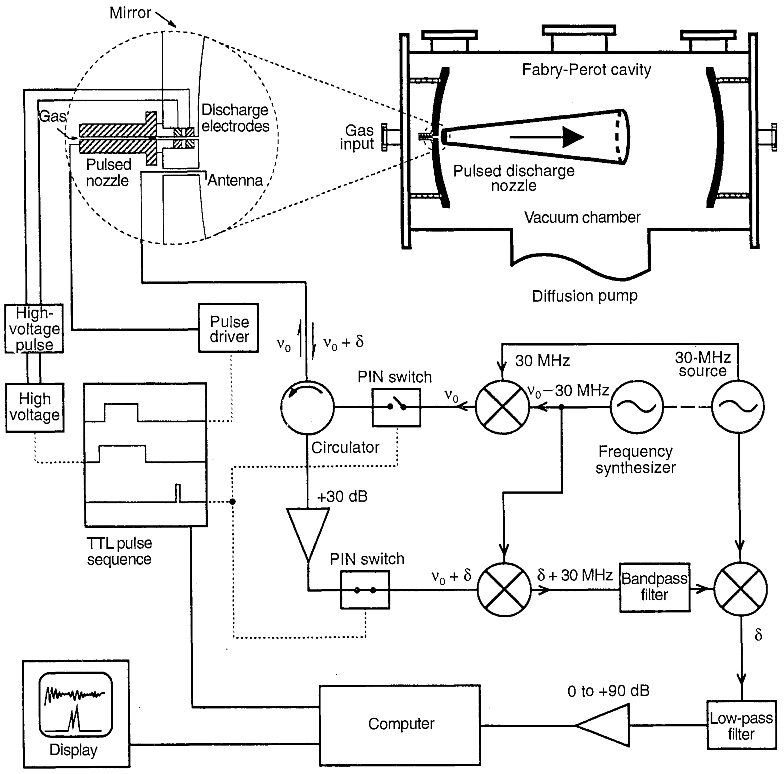

Fig. 1. The Fourier transform microwave spectrometer. A pulsed supersonic molecular beam of either dilute diacetylene (1%) or acetylene (1%) in Ne or in Ar is produced by a commercial solenoid valve (diameter 1 mm) operated by a pulse driver (General Valve). As the beam expands through the nozzle in one of the mirrors of the Fabry-Perot confocal cavity, a 1050-V discharge is applied synchronously with the 390-μs-long gas pulse; the discharge source consists of alternating layers of Cu electrodes and Teflon insulators. At a pressure of the mixture behind the pulsed valve of 2 atm, the discharge in the nozzle throat was stable and the rotational temperature of the molecules downstream in the supersonic beam was only a few kelvin. The production of H_2C_5 and H_2C_6 in our spectrometer is similar to that recently used for the C-chain radicals C_7H through $C_{11}H$ (*29*). As in the case of the C chain radicals, diacetylene yielded stronger signals than acetylene by about a factor of 2. As the molecular beam traverses the highly reflective confocal cavity (70 cm long and 36 cm in diameter), the molecules are irradiated with a short (1 μs) microwave pulse at a frequency ν_0 such that $|\nu_0 - \nu| \leq \Delta\nu/2$, where $\Delta\nu$ is the full width at half height when the Fabry-Perot is tuned to the resonant frequency at ν (that is, ν_0 lies within the bandwidth of the cavity). The subsequent free-induction decay is detected with a superheterodyne receiver. The Fourier transform of the free induction yields the power spectrum, which is then displayed as a frequency offset from the pump frequency ν_0. The vacuum chamber was maintained at a background pressure of 10^{-6} torr with a diffusion pump 14 inches in diameter (8000 liter/s, Varian) backed by a dual-stage mechanical pump (14 liter/s, Leybold); typical transient pressures were 5×10^{-5} torr at the 2-Hz repetition rate of the nozzle. Helmholtz coils were used to cancel Earth's magnetic field to within ±3%.

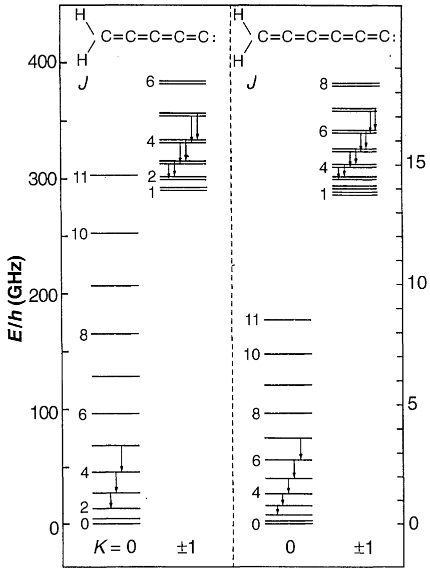

Fig. 2. Rotational energy levels of H_2C_5 and H_2C_6. The arrows indicate measured transitions. The energy scale is given in both frequency (E/h, left) and temperature (E/k, right), where E is energy, h is the Planck constant, and k is the Boltzmann constant. The transitions are grouped into closely spaced triplets: all have the same J, but each originates from a different K level (one from $K = 0$ and two from $K = \pm 1$). The frequency spacing between the lines is determined by the asymmetry doubling in the $K = \pm 1$ ladder.

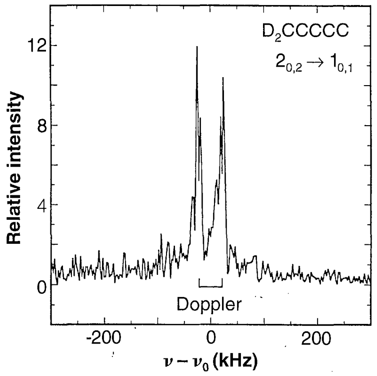

Fig. 3. Rotational transition of D_2C_5 at ν_0 = 8452.440 MHz, showing evidence for partially resolved deuterium quadrupole hyperfine structure. The double-peaked line shape is the result of the Doppler shift of the two traveling waves that compose the confocal mode of the Fabry-Perot cavity with respect to the molecular beam. This spectrum was obtained with an integration time of about 2 min.

strongest evidence is that the A rotational constants of H_2C_5 and H_2C_6 are within 4% of those of H_2C_3 (*7*) and H_2C_4 (*5*). Any bend or zigzag in the chain lowers A by displacing C atoms from the least principal axis of inertia; distortions by more than about 4° would lower A unacceptably, the exact limit depending on the nature of the assumed departure from linearity. Although expected on the basis of the valence structures, this is an interesting demonstration, because at least one similar molecule, H_2CCCO, is apparently bent (*13*), and in H_2C_3 and H_2C_4 the C–C–C bending potentials are quite shallow (*14, 15*).

By analogy with shorter members of the sequence, it might be expected that isomers of H_2C_5 and H_2C_6 can be found that are comparable in energy or even more stable than the carbenes described here. The rotational spectrum of H_2C_4 is readily observed, even though this carbene has been calculated to be higher in energy by ~2 eV than diacetylene (HC_4H) (*16*). The carbene H_2C_5 can be detected with a signal-to-noise ratio of >5 in less than 1 s of integration time with our FTM spectrometer, so other isomers may be readily detectable. Two interesting C_5H_2 isomers can be derived from cyclic C_3H_2, one by substituting the ethynyl radical C_2H for an H atom, the other by attaching C_2 to the carbene C. In recent quantum chemical calculations, McMahon (*17*) concluded that the former structure is more stable by ~0.5 eV than the cumulenic form observed here.

Carbenes play important roles in the combustion of hydrocarbon fuels and the formation of soot and other carbon compounds. In current kinetic and thermochemical models of O_2-acetylene-Ar flames, carbenes such as singlet and triplet methylene are central to the formation of larger hydrocarbons, including ones that ultimately lead to rings. Cumulene carbenes are probably produced in the polymerization of acetylene, but, because most chemical models (*18, 19*) do not distinguish between different isomers with the same elemental formula (for example, HC_4H and H_2C_4) and branching ratios are not known, the roles they play as intermediates remain unclear. Better understanding of the structure and chemical properties of carbene chains should clarify their role in combustion.

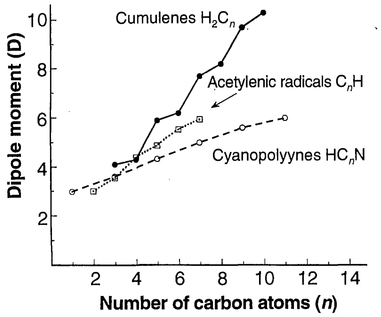

Fig. 4. Calculated dipole moment versus chain length for the cumulenic (*10*), acetylenic (*30*), and cyanopolyyne (*31*) C chains.

Both H_2C_3 and H_2C_4 were immediately discovered in space after laboratory detection; the carbenes described here may thus also be of interest in radio astronomy. Their calculated dipole moments (*10*), 5.9 D for H_2C_5 and 6.2 D for H_2C_6, are extremely large for hydrocarbons and even large compared to the values for other polar C chains of the same length (Fig. 4), several of which have been detected in astronomical sources. At comparable abundances, H_2C_5 and H_2C_6 should therefore be somewhat easier to detect.

Chemical models of interstellar clouds (*20*) predict that some carbenes are natural by-products in the production of more familiar stable molecules by both ion-molecule and neutral-neutral reactions. These models predict that carbene chains with an even number of C atoms are more abundant than those with an odd number, correctly accounting for the H_2C_4/H_2C_3 ratio in the circumstellar shell of the evolved C star IRC+10216 (*21, 22*) and implying that, of the two carbenes described here, H_2C_6 may be the most readily detected in astronomical sources. A plausible mechanism that could produce it in a dense molecular cloud is electron recombination of the $C_6H_3^+$ ion (which may be formed in several steps by reactions of acetylene with protonated acetylene $C_2H_3^+$ or the acetylene ion $C_2H_2^+$), yielding either H_2C_6 + H or triacetylene (HC_6H) + H.

In addition to their chemical and astrophysical interest, cumulene carbenes are possible carriers of the diffuse interstellar bands, the generally broad, featureless optical absorption lines scattered across the visible and infrared spectrum. Carbon chains are attractive candidates (*23*) because they constitute well over one-half of the polyatomic interstellar and circumstellar molecules identified to date and are expected to have conjugated structures that should give rise to intense electronic transitions (*24*). Detection of the gas-phase electronic spectra of cumulene chains 5 to 15 C atoms long may provide a crucial test for the C chain hypothesis. Ultraviolet absorption spectra of matrix-isolated H_2C_3 have been detected (*25*). We estimate the concentration of H_2C_6 to be 1×10^{10} molecules per gas pulse in our pulsed discharge beam on the basis of calibrations with 1% carbonyl sulfide (OCS) in Ar, which means that the electronic spectra of the known cumulene carbenes should be detectable by laser-induced fluorescence or resonant enhanced multiphoton ionization spectroscopy.

It is likely that longer cumulene carbenes can be observed at both microwave and optical wavelengths. The sensitivity of our FTM spectrometer is still quite far from its theoretical limit; refinements in the microwave receiver and in the production of reactive molecules, for example, may improve the sensitivity by an order of magnitude or more, which should be adequate to detect at least H_2C_7 and H_2C_8.

Note added in proof: On the basis of the laboratory data here, H_2C_6 has just been detected in the astronomical source TMC-1 (*26*).

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