

## LABORATORY DETECTION OF TWO NEW C<sub>5</sub>H<sub>2</sub> ISOMERS

C. A. GOTTLIEB,<sup>1</sup> M. C. MCCARTHY,<sup>1,2</sup> V. D. GORDON,<sup>1</sup> J. M. CHAKAN,<sup>1</sup> A. J. APPONI,<sup>1,2</sup> AND P. THADDEUS<sup>1,2</sup>

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### ABSTRACT

Two new isomers of the C<sub>5</sub>H<sub>2</sub> molecule have been detected in the laboratory, and their microwave spectra have been characterized to high accuracy. Both are good candidates for radio astronomical detection. Like the two isomers previously detected in the laboratory, both are closed-shell carbenes, and both are extremely polar and fairly stable. The first, calculated to lie 0.73 eV above isomer 1, the C<sub>5</sub>H<sub>2</sub> ring-chain ground state, has a bent carbon chain backbone with single, double, and triple bonds; the second, calculated to lie only 0.19 eV higher in energy, is a new type of ring chain formed by adding a pair of doubly bonded carbon atoms to the top of the C<sub>3</sub>H<sub>2</sub> ring, which is one of the most abundant interstellar molecules.

*Subject headings:* ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

The detection of energetic molecular isomers in dense interstellar clouds is a striking demonstration of the very large departures from chemical and thermal equilibrium that occur in space. A good example is HNC, which is less stable by about 0.6 eV, or 7000 K, than HCN but is nearly as abundant as this stable isomer in some molecular clouds in which the kinetic temperature is only a few tens of kelvins (Herbst 1978) and the thermal ratio HNC/HCN is nil ( $\sim 10^{-200}$ ). Ion-molecule chemistry provides a simple explanation for this arresting anomaly: both isomers are thought to be made at roughly comparable rates by the same reaction, the dissociative recombination of the ion HCNH<sup>+</sup>, a reaction that weakly couples the cold molecular gas to the very hot reservoir of cosmic rays which is largely responsible for the residual ionization in cold, dark gas. Nearly all subsequent collisions are with neutral particles, and these are not energetic enough to overcome the isomerization barrier and convert HNC to the more stable HCN. Because similar ion-molecule production paths may exist for many molecular isomers, it may be possible to find many more isomers of the over 115 molecules that have now been detected in space, once laboratory rest frequencies of these elusive molecules are in hand.

Isomeric systems with the elemental formula C<sub>5</sub>H<sub>2</sub> are of astronomical interest because of their simplicity and because much larger carbon molecules have been detected in molecular clouds and in circumstellar shells (e.g., HC<sub>11</sub>N; Bell et al. 1997). Two members of this system—the ring-chain isomer 1 in Figure 1, the most stable isomer according to quantum calculations (Seburg et al. 1997), and isomer 2, a molecule with a linear carbon backbone calculated to lie 0.6 eV higher in energy—have already been detected in this laboratory (Travers et al. 1997; McCarthy et al. 1997a), and astronomical searches are underway. Both are good candidates for astronomical detection because H<sub>2</sub>C<sub>4</sub> and H<sub>2</sub>C<sub>6</sub>, the shorter and longer members of the cumulene family of isomer 2, have already been detected in the expanding shell of the evolved carbon star IRC +10216 or in the rich molecular source TMC-1, or both (Langer et al. 1997). Here we report the laboratory detection and spectroscopic characterization of two more fairly low-lying and as-

tronomically interesting isomers of C<sub>5</sub>H<sub>2</sub>, those numbered 3 and 4 in Figure 1.

Like the previously detected isomers, these are highly polar carbenes, with two nonbonding electrons, as Figure 1 shows. Both are planar, nearly symmetric prolate tops with singlet electronic ground states. According to quantum ab initio calculations, the bent isomer 3 has a dipole moment of 4.8 D, and the symmetric isomer 4—dubbed by the quantum chemists eiffelene—is even more polar, with a dipole moment of 8.2 D, which is astonishingly large for a hydrocarbon molecule. For isomer 3, the dipole moment along the intermediate principal axis of inertia *b* is calculated to be 36% as large as that along the least principal axis *a* (J. F. Stanton 1998, private communication), so *b*-type as well as *a*-type rotational transitions can in principle be observed—although they are weaker by an order of magnitude. For isomer 4, owing to the C<sub>2v</sub> symmetry, only *a*-type transitions are permitted.

Both new isomers were identified in the centimeter-wave band with a very sensitive Fourier-transform microwave (FTM) spectrometer designed to study rotationally cold reactive molecules in a supersonic molecular beam (McCarthy et al. 1997b), a combination with which several dozen new carbon chains and other reactive molecules have recently been detected (Thaddeus et al. 1998). The observed rotational transitions are indicated in the energy-level diagrams of Figure 2; Table 1 gives the measured frequencies, and Table 2 gives the spectroscopic constants derived from them. For the bent isomer, only *a*-type transitions have so far been observed. As Table 2 shows, the rotational constants for both isomers are within 1% of those predicted by the ab initio structures with the exception of *A* in isomer 3 which differs by 2%, and this agreement alone makes it almost certain that the present assignments are correct. In addition, as a crucial check, we found that the rotational lines of the doubly deuterated isotopic species (from a D-enriched gas sample) occurred almost exactly at the large predicted isotope shifts (typically about 6% to lower frequency). Finally, as predicted for singlet molecules, the lines we assign have no appreciable Zeeman effect when a strong permanent magnet is brought near the supersonic beam of the spectrometer, and the lines, although approximately harmonic in frequency, are related by integer quantum numbers with a large harmonic defect, as expected for closed-shell molecules with nonlinear carbon backbones.

The elemental compositions of our new molecules are also

<sup>1</sup> Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138.

<sup>2</sup> Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138.

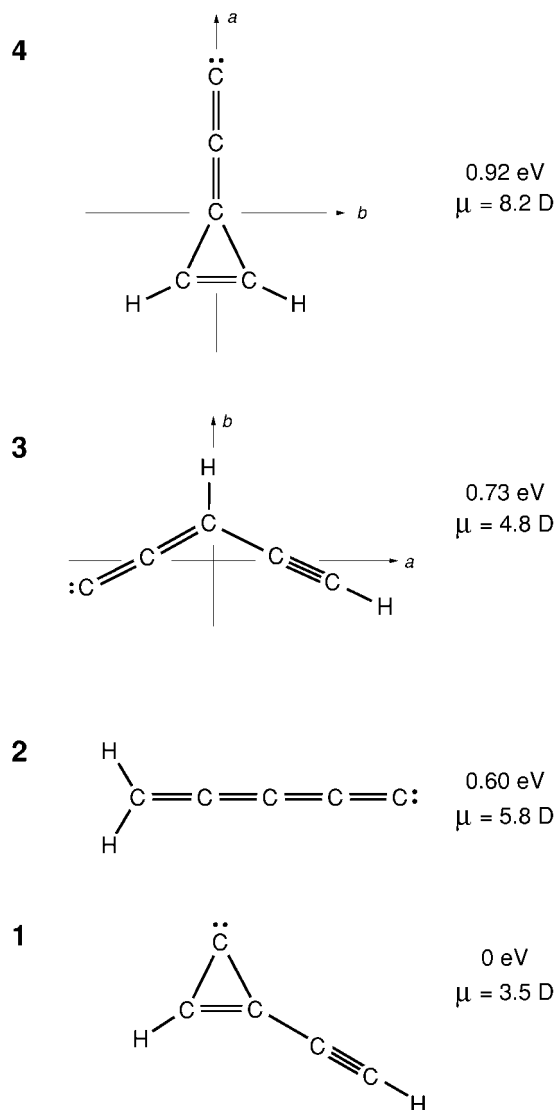


FIG. 1.—Four isomers of  $C_5H_2$  identified with the present FTM spectrometer; the two new ones are at the top. Double dots indicate the characteristic carbene nonbonding electrons. The listed dipole moments and energies relative to isomer 1 are the result of quantum ab initio calculations by Seburg et al. (1997).

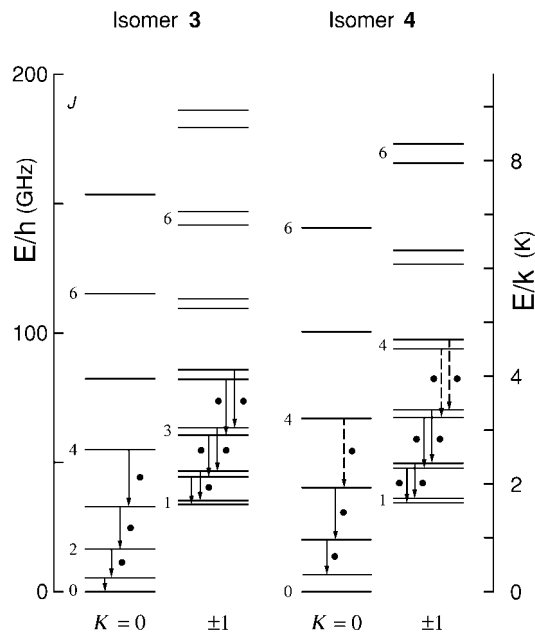


FIG. 2.—Lower rotational levels of isomers 3 and 4, showing the observed transitions. Solid arrows indicate transitions observed in the normal isotopic species; dots show those observed in the doubly deuterated species.

consistent with the assignments here. To demonstrate that we are observing pure hydrocarbons, several different precursor gases have been used in our discharge source. The strongest lines were obtained from a discharge through diacetylene ( $HC_4H$ ) and neon, yielding in 1 minute of integration a signal-to-noise ratio of about 20 for the bent isomer and about 6 for eiffelene. The source conditions required to optimize both isomers are very similar to those used to study the ring-chains  $C_5H_2$ ,  $C_7H_2$ , and  $C_9H_2$  and the cumulenes  $H_2C_4$ ,  $H_2C_5$ , and  $H_2C_6$ : a DC discharge in the throat of our supersonic nozzle of about 1400 V and 40 mA synchronized with a 140  $\mu s$  long gas pulse of dilute ( $\sim 0.25\%$ ) diacetylene in Ne at a backing pressure of 1–2 atm. When a mixture of allene ( $H_2C_3H_2$ , an exceptionally good source of  $c\text{-}C_3H_2$ ) and acetylene (0.5% each) in Ne was used, signals of isomer 4 were about the same intensity as those from diacetylene alone. No evidence of lines from either isomer was observed with a discharge through only Ar or Ne, ruling out possible impurities in the buffer gases. As was the case with the detection of the  $C_5H_2$  ring chain (isomer 1, Fig. 1),

TABLE 1  
MEASURED ROTATIONAL FREQUENCIES OF  $C_5H_2$  AND  $C_5D_2$  ISOMERS

TRANSITION	ISOMER 3				ISOMER 4			
	$C_5H_2$		$C_5D_2$		$C_5H_2$		$C_5D_2$	
	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)	Frequency (MHz)	$O - C$ (kHz)
$1_{0,1} \rightarrow 0_{0,0}$ .....	5490.247	0	...	...	...	...	...	...
$2_{1,2} \rightarrow 1_{1,1}$ .....	10739.735	0	...	...	13060.510	0	12151.703	-2
$2_{0,2} \rightarrow 1_{0,1}$ .....	10978.956	0	10299.138	0	13410.659	0	12554.053	0
$2_{1,1} \rightarrow 1_{1,0}$ .....	11222.297	-1	10567.534	-2	13767.097	0	...	...
$3_{1,3} \rightarrow 2_{1,2}$ .....	16108.601	0	15052.704	0	19588.715	0	18223.866	0
$3_{0,3} \rightarrow 2_{0,2}$ .....	16464.592	0	15442.810	0	20107.800	0	18816.252	0
$3_{1,2} \rightarrow 2_{1,1}$ .....	16832.396	1	15849.743	0	20648.578	0	19448.321	2
$4_{1,4} \rightarrow 3_{1,3}$ .....	21476.273	0	20067.492	0	...	...	24291.675	1
$4_{0,4} \rightarrow 3_{0,3}$ .....	21945.622	0	20579.418	0	...	...	25060.707	0
$4_{1,3} \rightarrow 3_{1,2}$ .....	22441.222	0	21130.059	0	...	...	25924.025	-2

NOTE.—Estimated measurement uncertainty: 2–5 kHz.

TABLE 2  
 ROTATIONAL AND CENTRIFUGAL DISTORTION CONSTANTS OF C<sub>5</sub>H<sub>2</sub> AND C<sub>5</sub>D<sub>2</sub> ISOMERS (IN MHz)

CONSTANT	ISOMER 3				ISOMER 4			
	C <sub>5</sub> H <sub>2</sub>		C <sub>5</sub> D <sub>2</sub>		C <sub>5</sub> H <sub>2</sub>		C <sub>5</sub> D <sub>2</sub>	
	Measured <sup>a</sup>	Expected	Measured <sup>a</sup>	Expected	Measured <sup>a</sup>	Expected	Measured <sup>a</sup>	Expected
<i>A</i> .....	31816(6)	32482 <sup>b</sup>	25302(2)	25894 <sup>b</sup>	31979(6)	32080 <sup>b</sup>	24211(3)	24314 <sup>b</sup>
<i>B</i> .....	2865.7729(3)	2843 <sup>b</sup>	2708.2336(3)	2685 <sup>b</sup>	3530.1312(2)	3529 <sup>b</sup>	3344.0816(5)	3342 <sup>b</sup>
<i>C</i> .....	2624.4795(3)	2614 <sup>b</sup>	2442.5201(2)	2433 <sup>b</sup>	3176.8374(2)	3179 <sup>b</sup>	2935.9127(5)	2938 <sup>b</sup>
$\Delta_J \times 10^3$ .....	1.471(8)	0.288 <sup>c</sup>	1.239(6)	0.174 <sup>c</sup>	0.246(17)	0.288 <sup>c</sup>	0.184(21)	0.174 <sup>c</sup>
$\Delta_{JK}$ .....	-0.1397(2)	0.0295 <sup>c</sup>	-0.0920(2)	0.024 <sup>c</sup>	0.0314(3)	0.0295 <sup>c</sup>	0.0273(6)	0.024 <sup>c</sup>
$\delta_J \times 10^3$ .....	0.371(6)	...	0.411(4)	...	...	...	...	...
$\Delta^d$ .....	0.329(3)	0.160 <sup>c</sup>	0.327(1)	0.177 <sup>c</sup>	0.117(3)	0.160 <sup>c</sup>	0.136(2)	0.177 <sup>c</sup>

NOTE—Uncertainties (1  $\sigma$ ) are in units of the last significant digit.

<sup>a</sup> Derived from a least-squares fit of Watson's *A*-reduced Hamiltonian to the data in Table 1.

<sup>b</sup> From a CCSD(T)/cc-pVTZ ab initio calculation of Seburg et al. 1997.

<sup>c</sup> From measurements of C<sub>5</sub>H<sub>2</sub> isomer 1 (Travers et al. 1997).

<sup>d</sup> The inertial defect,  $\Delta = I_C - I_A - I_B$ .

oxygen-containing impurities cannot be absolutely excluded, since there may be small traces of water or molecular oxygen in our gas sample; but no plausible candidates containing oxygen have been found, and lines of known oxygen-containing molecules are either very weak or absent. Owing to our high spectral resolution, well-resolved quadrupole hyperfine structure (hfs) with splittings of the order of 1 MHz would have been detected if either isomer contained nitrogen.

As Figure 3 shows, however, there is evidence for barely resolved quadrupole hfs of the amount expected from the deuterons in the doubly deuterated species—structure that further confirms the assignment. On the standard assumption that the internal electric field of isomer 4 is cylindrically symmetric about the C—D bond, we find that the deuteron quadrupole coupling constant along the bond  $\chi_{zz}$  is  $266 \pm 30$  kHz, which agrees reasonably well with that found for other molecules with C—D bonds. That for cyclopropenyldene (C<sub>3</sub>HD) for example,

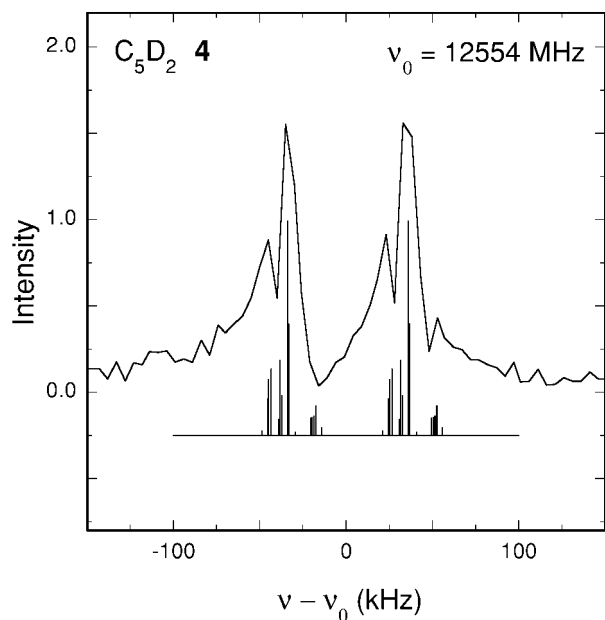


FIG. 3.—Observed  $2_{02}-1_{01}$  transition of doubly deuterated isomer 4, with partially resolved quadrupole hfs from the deuterons. The large doublet structure is instrumental in origin, the result of the Doppler shift of the Mach 2 jet relative to the two travelling waves that compose the confocal mode of the Fabry-Perot resonator.

as derived from observations of TMC-1, is  $186.9 \pm 1.4$  kHz (Bell et al. 1987).

The possibility of detecting a quasi-linear triplet isomer of C<sub>5</sub>H<sub>2</sub> is intriguing because according to quantum calculations this isomer is slightly more stable, by about 2 kcal or 0.1 eV, than the most stable singlet system, isomer 1 (Seburg et al. 1997). The quantum calculations, however, indicate that there is no minimum in the triplet potential energy surface corresponding to a bent geometry (as would be obtained by substituting a linear C<sub>4</sub>H chain for one of the hydrogen atoms of methylene) and that therefore this isomer is nonpolar, without a radio spectrum. This conclusion is worth reexamination because a polar configuration would produce a nearly harmonic rotational spectrum with lines in the centimeter band very favorable for observation both in the laboratory and in space.

Although it is difficult for us to estimate relative stabilities of isomers from line strengths, the intensities of the four C<sub>5</sub>H<sub>2</sub> isomers approximately correlate with the relative energies predicted from recent theoretical calculations by Seburg et al. (1997). Near 13 GHz, the  $K_a = 0$  lines of the four isomers (in energy ordering) are in the ratio of about 100:25:15:1. Relative abundances, obtained from the line intensities by taking into account the dependence on the chain length of the rotational partition function, dipole moments, and nuclear spin statistics, are 165:35:10:1. Although each isomer is presumably made via different sets of reactions, the fairly close correlation of abundance with relative energy suggests that it should be possible to observe other fairly energetic isomers of many carbon chains, including exotic isomers of almost all of our more than two dozen new chains (Thaddeus et al. 1998).

Because molecules comparable in size to C<sub>5</sub>H<sub>2</sub> tend to have strong lines in the millimeter-wave band, well above the region covered by the present measurements, we list in Table 3 to above 110 GHz the frequencies for the *a*-type transitions of the lowest three  $K_a$  ladders of the new isomers calculated from the spectroscopic constants in Table 2. With these we have attempted to find those isomers in radio spectral line surveys of the best molecular sources—so far without success. In the extensive survey of IRC +10216 by Kawaguchi et al. (1995), for example, 3  $\sigma$  upper limits of 10 mK can be set for the strongest expected lines from Table 3. On the assumption of optically thin lines, a rotational temperature of 20 K, and the dipole moments listed in Figure 1, we find upper limits on the column densities of isomers 3 and 4 of  $2 \times 10^{13}$  and  $5 \times 10^{12}$  cm<sup>-2</sup>, respectively—the better limit in the second case

TABLE 3  
 CALCULATED *a*-TYPE ROTATIONAL TRANSITIONS OF C<sub>3</sub>H<sub>2</sub> ISOMERS (IN MHz)<sup>a</sup>

Transition	Isomer 3	Isomer 4	Transition	Isomer 3	Isomer 4
1 <sub>0,1</sub> → 0 <sub>0,0</sub> .....	5490.246	6706.968	11 <sub>0,11</sub> → 10 <sub>0,10</sub> .....	60059.965	73076.797
2 <sub>1,2</sub> → 1 <sub>1,1</sub> .....	10739.735	13060.511	11 <sub>1,10</sub> → 10 <sub>1,9</sub> .....	61629.072	75530.008
2 <sub>0,2</sub> → 1 <sub>0,1</sub> .....	10978.956	13410.659	12 <sub>1,12</sub> → 11 <sub>1,11</sub> .....	64331.966	78150.828
2 <sub>1,1</sub> → 1 <sub>1,0</sub> .....	11222.298	13767.098	12 <sub>0,12</sub> → 11 <sub>0,11</sub> .....	65452.965	79584.422
3 <sub>1,3</sub> → 2 <sub>1,2</sub> .....	16108.601	19588.717	12 <sub>1,11</sub> → 11 <sub>1,10</sub> .....	67210.759	82352.703
3 <sub>0,3</sub> → 2 <sub>0,2</sub> .....	16464.592	20107.801	13 <sub>1,13</sub> → 12 <sub>1,12</sub> .....	69673.691	84626.266
3 <sub>1,2</sub> → 2 <sub>1,1</sub> .....	16832.395	20648.578	13 <sub>0,13</sub> → 12 <sub>0,12</sub> .....	70830.006	86062.773
4 <sub>1,4</sub> → 3 <sub>1,3</sub> .....	21476.273	26114.490	13 <sub>1,12</sub> → 12 <sub>1,11</sub> .....	72786.619	89162.734
4 <sub>0,4</sub> → 3 <sub>0,3</sub> .....	21945.622	26795.127	14 <sub>1,14</sub> → 13 <sub>1,13</sub> .....	75011.256	91094.141
4 <sub>1,3</sub> → 3 <sub>1,2</sub> .....	22441.222	27527.551	14 <sub>0,14</sub> → 13 <sub>0,13</sub> .....	76190.619	92512.648
5 <sub>1,5</sub> → 4 <sub>1,4</sub> .....	26842.369	32637.063	14 <sub>1,13</sub> → 13 <sub>1,12</sub> .....	78356.019	95958.547
5 <sub>0,5</sub> → 4 <sub>0,4</sub> .....	27420.522	33469.398	15 <sub>1,15</sub> → 14 <sub>1,14</sub> .....	80344.509	97554.359
5 <sub>1,4</sub> → 4 <sub>1,3</sub> .....	28048.343	34403.133	15 <sub>0,15</sub> → 14 <sub>0,14</sub> .....	81534.622	98935.648
6 <sub>1,6</sub> → 5 <sub>1,5</sub> .....	32206.517	39155.707	15 <sub>1,14</sub> → 14 <sub>1,13</sub> .....	83918.290	102738.438
6 <sub>0,6</sub> → 5 <sub>0,5</sub> .....	32887.784	40127.445	16 <sub>1,16</sub> → 15 <sub>1,15</sub> .....	85673.330	104006.883
6 <sub>1,5</sub> → 5 <sub>1,4</sub> .....	33653.310	41274.410	16 <sub>0,16</sub> → 15 <sub>0,15</sub> .....	86862.147	105334.148
7 <sub>1,7</sub> → 6 <sub>1,6</sub> .....	37568.361	45669.734	16 <sub>1,15</sub> → 15 <sub>1,14</sub> .....	89472.729	109500.641
7 <sub>0,7</sub> → 6 <sub>0,6</sub> .....	38345.928	46766.215	17 <sub>1,17</sub> → 16 <sub>1,16</sub> .....	90997.631	110451.773
7 <sub>1,6</sub> → 6 <sub>1,5</sub> .....	39255.663	48140.406	17 <sub>0,17</sub> → 16 <sub>0,16</sub> .....	92173.645	111711.094
8 <sub>1,8</sub> → 7 <sub>1,7</sub> .....	42927.564	52178.516	17 <sub>1,16</sub> → 16 <sub>1,15</sub> .....	95018.597	116243.281
8 <sub>0,8</sub> → 7 <sub>0,7</sub> .....	43793.525	53382.852	18 <sub>1,18</sub> → 17 <sub>1,17</sub> .....	96317.355	116889.141
8 <sub>1,7</sub> → 7 <sub>1,6</sub> .....	44854.924	55000.102	18 <sub>0,18</sub> → 17 <sub>0,17</sub> .....	97469.872	118069.820
9 <sub>1,9</sub> → 8 <sub>1,8</sub> .....	48283.807	58681.480	18 <sub>1,17</sub> → 17 <sub>0,16</sub> .....	100555.120	122964.406
9 <sub>0,9</sub> → 8 <sub>0,8</sub> .....	49229.212	59974.813	19 <sub>1,19</sub> → 18 <sub>1,18</sub> .....	101632.477	123319.180
9 <sub>1,8</sub> → 8 <sub>1,7</sub> .....	50450.596	61852.398	19 <sub>0,19</sub> → 18 <sub>0,18</sub> .....	102751.866	124413.797
10 <sub>1,10</sub> → 9 <sub>1,9</sub> .....	53636.797	65178.129	19 <sub>1,18</sub> → 18 <sub>0,17</sub> .....	106081.494	129662.031
10 <sub>0,10</sub> → 9 <sub>0,9</sub> .....	54651.733	66539.977	20 <sub>1,20</sub> → 19 <sub>1,19</sub> .....	106942.999	129742.133
10 <sub>1,9</sub> → 9 <sub>1,8</sub> .....	56042.160	68696.125	20 <sub>0,20</sub> → 19 <sub>0,19</sub> .....	108020.893	130746.461
11 <sub>1,11</sub> → 10 <sub>1,10</sub> .....	58986.264	71668.031	20 <sub>1,19</sub> → 19 <sub>0,18</sub> .....	111596.882	136334.203

<sup>a</sup> Accuracy is 0.3 ppm or better.

resulting mainly from the significantly larger dipole moment. Deliberate searches at specific frequencies with existing radio telescopes could probably improve these limits by at least a factor of 3.

Eiffelene is of general interest as the first detected member of a hypothetical family of new carbon ring-chain molecules derived from the three-member ring C<sub>3</sub>H<sub>2</sub>. The previous five ring chains detected with the present FTM spectrometer are all derived by substituting acetylenic carbon chains or carbon-nitrogen chains for one of the hydrogen atoms of C<sub>3</sub>H<sub>2</sub>. Several years ago, we searched unsuccessfully with our free space millimeter-wave spectrometer for the first member of this new family, the carbene isomer of diacetylene (HCCCCH) obtained by removing one of the two carbon atoms at the top of eiffelene;

this failure may be the result of the high energy of this isomer relative to diacetylene: 3.5 eV according to Collins et al. (1992). Only one line of this molecule, the 1<sub>0,1</sub>-0<sub>0,0</sub> transition estimated to lie at about 14.770 GHz, is expected to lie within the current operating range of our FTM spectrometer, so identification without an expansion of spectral range is hardly possible. Eiffelenes longer than C<sub>3</sub>H<sub>2</sub> will have many lines within our current band, and several may be detectable with our current level of sensitivity, but to our knowledge quantum calculations to guide a search have not been done for any of these.

Quantum chemical calculations have been very useful to this investigation. We are particularly indebted to the work of R. J. McMahon, J. F. Stanton, and their collaborators.

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