Structure of propadienylidene, H_2CCC

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The millimeter-wave rotational spectra of four isotopic species of the cumulene carbene propadienylidene ($H_2{}^{13}CCC$, $H_2C^{13}CC$, $H_2CC^{13}C$, and D_2CCC) were measured and the same set of rotational and centrifugal distortion constants used to describe the normal species [Vrtilek *et al.*, Astrophys. J. Lett. **364**, L53 (1990)] were determined, allowing the r_0 and r_s structures to be derived. Vibration–rotation coupling constants calculated *ab initio* in the CEPA-1 approximation were combined with the experimental rotational constants for the four isotopic species and the normal species to yield the equilibrium geometry: $r_e(HC_{(1)}) = 1.083 \pm 0.001$ Å, $r_e(C_{(1)}C_{(2)}) = 1.3283 \pm 0.0005$ Å, $r_e(C_{(2)}C_{(3)}) = 1.291 \pm 0.001$ Å, and $\angle\,(HC_{(1)}H) = 117.6 \pm 0.2°$. The calculated spectroscopic properties may aid forthcoming high-resolution IR spectroscopy of H_2CCC.

I. INTRODUCTION

The free cumulene carbene propadienylidene, H_2CCC, was recently detected in the laboratory[1] and in the interstellar gas,[2] by observations of its millimeter-wave rotational spectrum. Propadienylidene is a near prolate top with C_{2v} symmetry (Fig. 1), a singlet electronic ground state and large dipole moment (4.14 D); it is calculated[3] to be 0.63 eV less stable than the three-membered carbene ring cyclopropenylidene with the same elemental formula, previously identified in both laboratory and astronomical sources.[4] The rotational spectrum of H_2CCC is very similar to that of the stable molecules ketene and formaldehyde—geometrically similar molecules also with the same C_{2v} symmetry and two off-axis equivalent hydrogen atoms.

To determine the geometrical structure of H_2CCC we have now investigated the millimeter-wave spectrum of four of its isotopic species: the three obtained by substituting ^{13}C for each of the carbon in turn, plus D_2CCC. For each isotopic species, a sufficient number of rotational transitions were observed to allow determination of the three rotational constants and the leading centrifugal distortion constants. The zero point (r_0) structure[5] and substitution (r_s) structure[6] were determined from the experimental data. Determination of an accurate equilibrium structure is possible through the combination of experimental and theoretical data. Following the pioneering work of Pulay *et al.* on methane[7] we have calculated the vibration–rotation coupling constants of H_2CCC *ab initio* in order to convert the measured ground state rotational constants to equilibrium constants. More details of the approach are given in Sec. IV C. The experimental part of the present investigation was done at Cambridge and the theoretical work at Göttingen.

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II. EXPERIMENT

The rotational spectra of the isotopic species of H_2CCC were measured with the same free space millimeter-wave spectrometer used for the normal species.[8] Free H_2CCC was produced in a dc discharge (~0.5 A) through acetylene, carbon monoxide, and helium (in molar ratios of approximately 50:20:1) at a temperature of 150 K and pressure of about 20 mTorr. Although H_2CCC was first observed in a discharge through acetylene and helium, its concentration was found to increase by a factor of 3 on adding the specified amount of CO. The ^{13}C species were observed when ^{12}CO was replaced by 99.1% ^{13}C enriched carbon monoxide (Isotec). Similarily, D_2CCC was produced by replacing normal acetylene by deuterated acetylene synthesized by dripping D_2O onto calcium carbide. Lines of the ^{13}C species were about six times weaker than corresponding lines of the normal species. The nearly equal concentration of $H_2{}^{13}CCC$, $H_2C^{13}CC$ and $H_2CC^{13}C$ which we observe implies that the odd C atom, arising from partial dissociation of CO, entered all three positions in the carbon-chain backbone of H_2CCC with roughly equal probability.

III. RESULTS AND ANALYSIS

Fifty millimeter- and submillimeter-wave *a*-type *R*-branch ($\Delta J = 1$) transitions were measured for D_2CCC (Table I); owing to the cost of the enriched ^{13}CO, somewhat fewer were measured for each of the three singly substituted ^{13}C species (Table II). Only $\Delta K_a = 0$ lines were observed because H_2CCC is such a highly prolate asymmetric top ($\kappa = -0.9972$) that the $\Delta K_a = 2$ cross-ladder transitions (useful because they provide an accurate determination of the large rotational constant A) are more than 10^5 times weaker, and therefore well below our detection limit. The transition frequencies were analyzed with Watson's *S*-reduced Hamiltonian,[9] appropriate for near symmetric top molecules. Eight centrifugal distortion constants—the same determined for the normal species[1]—

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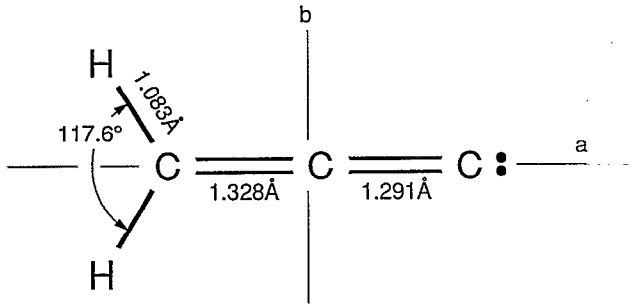

FIG. 1. The equilibrium geometry of H_2CCC obtained from the rotational constants of five isotopic species and vibration–rotation coupling constants calculated *ab initio*—the final result of the present investigation.

were determined for each of the isotopic species (Table III). Unlike the normal species, lines of the isotopic species were generally measured only once so measurement uncertainties are somewhat higher than previously (typically 25 kHz vs 15 kHz), but still only of order 0.1 ppm. The rms of the fits were 36 kHz for D_2CCC, and only slightly higher ($\sim$50 kHz) for the ^{13}C species. The observed rotational constants were transformed to Watson's determinable constants[9] (Table IV) by applying small ($\sim$0.5 MHz) corrections due to centrifugal distortion effects.

Although rotational constants B and C were determined to 1 part in 10^6 or better, A was not as well determined because (1) as mentioned, $\Delta K_a=2$ transitions could not be detected, (2) owing to its high correlation with A, the fourth-order distortion constant D_K could not be determined from our millimeter-wave data alone, and (3) A is very sensitive to distortion constant d_2 which is also highly correlated (correlation coefficient $\approx$0.9). In normal and deuterated ketene, D_K has been determined from a combined analysis of $\Delta K_a=0$ millimeter-wave rotational transitions and $\Delta K_a=2$ vibrational transitions observed in the IR.[10,11] The $\Delta K_a=2$ millimeter-wave rotational transitions have been observed in formaldehyde allowing A and D_K to be determined from the ground state rotational spectrum.[12] For H_2CCC and D_2CCC, we constrained D_K to the values in normal and deuterated ketene respectively, whereas in each of the ^{13}C species we constrained it to the value in normal ketene because D_K has not been determined for $H_2{}^{13}CCO$ and $H_2C{}^{13}CO$. If, by analogy with formaldehyde,[12] D_K changes by only 1% upon ^{13}C substitution in H_2CCC, the uncertainty in A for the ^{13}C species due to uncertainty in D_K is negligible. Estimates of D_K for H_2CCC derived from the *ab initio* quadratic force constants (Sec. IV C), imply that D_K for H_2CCC probably differs from that of H_2CCO by about 1.5 MHz. If so, the uncertainty in D_K introduces an uncertainty in A of only $\sim$3 MHz in the normal and ^{13}C isotopic species (i.e., much less than derived from the least-squares fits of the Hamiltonian to the measurements). In D_2CCC, however, similar estimates imply an uncertainty in A of 1.4 MHz and an overall uncertainty of 2.8 MHz (i.e., slightly higher than quoted in Table III).

TABLE I. Rotational transitions of D_2CCC.

Transition J_{K_a,K_c} (upper←lower)	Frequencies (MHz) Measured	O−C
$9_{4,6}\leftarrow 8_{4,5}$	163 889.521(15)	0.019
$9_{4,5}\leftarrow 8_{4,4}$		0.014
$9_{2,8}\leftarrow 8_{2,7}$	163 919.445(15)	0.023
$9_{3,7}\leftarrow 8_{3,6}$	163 950.744(30)[a]	−0.005
$9_{3,6}\leftarrow 8_{3,5}$		−0.005
$10_{4,7}\leftarrow 9_{4,6}$	182 101.132(20)	0.026
$10_{4,6}\leftarrow 9_{4,5}$		0.015
$10_{2,9}\leftarrow 9_{2,8}$	182 120.504(20)	0.023
$10_{3,8}\leftarrow 9_{3,7}$	182 172.617(30)[a]	0.066
$10_{3,7}\leftarrow 9_{3,6}$		−0.075
$11_{0,11}\leftarrow 10_{0,10}$	200 000.960(15)	0.015
$11_{4,8}\leftarrow 10_{4,7}$	200 313.287(15)	0.053
$11_{4,7}\leftarrow 10_{4,6}$		0.032
$11_{2,10}\leftarrow 10_{2,9}$	200 317.743(15)	0.056
$11_{3,9}\leftarrow 10_{3,8}$	200 393.805(30)	0.107
$11_{3,8}\leftarrow 10_{3,7}$	200 398.515(30)	−0.004
$11_{2,9}\leftarrow 10_{2,8}$	200 729.391(15)	0.020
$11_{1,10}\leftarrow 10_{1,9}$	203 516.929(20)	−0.043
$13_{3,11}\leftarrow 12_{3,10}$	236 842.955(20)	−0.016
$13_{3,10}\leftarrow 12_{3,9}$	236 854.154(20)	−0.061
$14_{1,13}\leftarrow 13_{1,12}$	258 919.766[b]	
$17_{1,17}\leftarrow 16_{1,16}$	304 358.410(10)	−0.002
$17_{0,17}\leftarrow 16_{0,16}$	308 188.758(10)	−0.032
$17_{2,16}\leftarrow 16_{2,15}$	309 398.502(10)	−0.033
$17_{5,13}\leftarrow 16_{5,12}$	309 442.809(10)	−0.014
$17_{5,12}\leftarrow 16_{5,11}$		−0.016
$17_{4,14}\leftarrow 16_{4,13}$	309 599.951(30)[a]	−0.069
$17_{4,13}\leftarrow 16_{4,12}$		−0.067
$17_{3,15}\leftarrow 16_{3,14}$	309 758.533(15)	0.007
$17_{3,14}\leftarrow 16_{3,13}$	309 801.942(10)	−0.034
$19_{2,18}\leftarrow 18_{2,17}$	345 710.659(10)	−0.028
$19_{5,15}\leftarrow 18_{5,14}$	345 849.332(10)	−0.017
$19_{5,14}\leftarrow 18_{5,13}$		−0.025
$19_{4,16}\leftarrow 18_{4,15}$	346 035.532(30)[a]	−0.010
$19_{4,15}\leftarrow 18_{4,14}$		−0.009
$19_{3,17}\leftarrow 18_{3,16}$	346 224.169(10)	−0.028
$19_{3,16}\leftarrow 18_{3,15}$	346 300.163(10)	0.063
$20_{1,20}\leftarrow 19_{1,19}$	357 891.787(15)	0.033
$20_{0,20}\leftarrow 19_{0,19}$	361 908.697(10)	0.004
$20_{2,19}\leftarrow 19_{2,18}$	363 856.081(10)	0.036
$20_{5,16}\leftarrow 19_{5,15}$	364 052.834(10)	0.039
$20_{5,15}\leftarrow 19_{5,14}$		0.028
$20_{4,17}\leftarrow 19_{4,16}$	364 254.717(30)[a]	−0.068
$20_{4,16}\leftarrow 19_{4,15}$		−0.061
$20_{3,18}\leftarrow 19_{3,17}$	364 458.667(10)	−0.005
$20_{3,17}\leftarrow 19_{3,16}$	364 556.837[b]	
$20_{2,18}\leftarrow 19_{2,17}$	366 256.732(10)	−0.012
$20_{1,19}\leftarrow 19_{1,18}$	369 471.684(10)	0.019

Note: Calculated frequencies are derived from the constants in Table III.
[a]Due to significant but not accurately measureable splittings of these partially blended K_a doublets, they were entered into the fit as two lines with the centroid at the measured frequency and the splitting set to a value calculated from other lines.
[b]Not included in fit because accurate frequencies are unobtainable.

TABLE II. Rotational transitions of $H_2{}^{13}CCC$, $H_2C^{13}CC$, and $H_2CC^{13}C$.

Transition	$H_2{}^{13}CCC$		$H_2C^{13}CC$		$H_2CC^{13}C$	
J_{K_a,K_c} (upper←lower)	Frequencies (MHz) Measured	O−C	Frequencies (MHz) Measured	O−C	Frequencies (MHz) Measured	O−C
$13_{1,13}\leftarrow12_{1,12}$	260 091.690(15)	0.080	267 625.688(15)	0.006	···	
$13_{0,13}\leftarrow12_{0,12}$	···		270 025.521(20)	−0.015	···	
$13_{4,10}\leftarrow12_{4,9}$ $13_{4,9}\leftarrow12_{4,8}$	262 286.877(30)	0.030 0.029	···		···	
$13_{3,11}\leftarrow12_{3,10}$ $13_{3,10}\leftarrow12_{3,9}$	···		270 065.800(20)[a]	−0.002 −0.001	···	
$13_{2,12}\leftarrow12_{2,11}$	···		270 094.154(20)	0.081	···	
$13_{2,11}\leftarrow12_{2,10}$	···		270 237.434(15)	−0.015	···	
$13_{1,12}\leftarrow12_{1,11}$	···		272 616.988(15)	0.022	262 294.444(30)	0.060
$14_{1,14}\leftarrow13_{1,13}$	···		288 199.985(15)	0.009	···	
$14_{4,11}\leftarrow13_{4,10}$ $14_{4,10}\leftarrow13_{4,9}$	···		290 713.697[b]		···	
$14_{0,14}\leftarrow13_{0,13}$	···		290 765.199(30)	−0.125	···	
$14_{3,10}\leftarrow13_{3,11}$ $14_{3,11}\leftarrow13_{3,10}$	···		290 836.998(20)[a]	0.006 0.007	···	
$14_{2,13}\leftarrow13_{2,12}$	···		290 860.136(20)	−0.009	···	
$14_{1,13}\leftarrow13_{1,12}$	···		293 574.468(15)	−0.011	···	
$15_{1,15}\leftarrow14_{1,14}$	300 080.511(10)	−0.029	···		297 284.707(15)	0.014
$15_{4,12}\leftarrow14_{4,11}$ $15_{4,11}\leftarrow14_{4,10}$	302 628.823(30)	−0.012 −0.015	311 473.456(20)	−0.005 −0.009	299 780.418(15)	−0.018 −0.021
$15_{0,15}\leftarrow14_{0,14}$	302 664.543(15)	0.022	311 498.192(30)	0.033	299 823.880(20)	−0.036
$15_{3,13}\leftarrow14_{3,12}$ $15_{3,12}\leftarrow14_{3,11}$	302 753.734[b]		···		299 905.308[b]	
$15_{2,14}\leftarrow14_{2,13}$	302 772.733[b]		311 623.751(30)	−0.156	299 926.344(20)	0.018
$15_{2,13}\leftarrow14_{2,12}$	302 969.310(15)	0.002	311 844.345(40)	0.012	300 115.442(30)	0.044
$15_{1,14}\leftarrow14_{1,13}$	305 517.713(20)	−0.020	···		302 621.471(10)	−0.004
$16_{1,16}\leftarrow15_{1,15}$	320 071.072(10)	−0.017	···		···	
$16_{4,13}\leftarrow15_{4,12}$ $16_{4,12}\leftarrow15_{4,11}$	322 798.075[b]		···		319 760.121(30)	−0.004 −0.008
$16_{0,16}\leftarrow15_{0,15}$	322 805.013(20)	−0.012	···		319 776.230(15)	−0.028
$16_{3,14}\leftarrow15_{3,13}$ $16_{3,13}\leftarrow15_{3,12}$	322 933.172[b]		···		319 893.853(40) 319 895.470(40)	0.059 −0.013
$16_{2,15}\leftarrow15_{2,14}$	322 944.903(20)	−0.071	···		···	
$16_{2,14}\leftarrow15_{2,13}$	323 183.460(30)	−0.013	···		320 138.483(30)	−0.079
$16_{1,15}\leftarrow15_{1,14}$	325 869.842(10)	0.030	···		···	
$17_{1,17}\leftarrow16_{1,16}$	340 058.957[b]		349 905.883(10)	0.002	···	
$17_{0,17}\leftarrow16_{0,16}$	···		352 941.077(40)	0.026	339 721.730(20)	0.045
$17_{4,14}\leftarrow16_{4,13}$ $17_{4,13}\leftarrow16_{4,12}$	···		352 990.537(30)	0.018 0.008	339 738.797(20)	0.084 0.076
$17_{3,15}\leftarrow16_{3,14}$	343 110.533[b]		···		339 882.388[b]	
$17_{3,14}\leftarrow16_{3,13}$	343 112.742[b]		···		339 885.289[b]	
$17_{2,16}\leftarrow16_{2,15}$	343 114.623[b]		···		339 889.408(30)	−0.005
$17_{2,15}\leftarrow16_{2,14}$	343 400.668(30)	−0.066	353 464.706(30)	−0.014	···	
$17_{1,16}\leftarrow16_{1,15}$	346 218.746(15)	−0.064	356 428.638(15)	0.009	···	
$18_{1,18}\leftarrow17_{1,17}$	···		···		356 689.882(15)	0.003
$18_{0,18}\leftarrow17_{0,17}$	363 064.211(20)	0.044	···		···	
$18_{4,15}\leftarrow17_{4,14}$ $18_{4,14}\leftarrow17_{4,13}$	363 133.733(30)	−0.002 −0.014	···		359 716.096(20)	−0.039 −0.050
$18_{2,17}\leftarrow17_{2,16}$	363 281.783(30)	0.018	···		359 867.170(30)	−0.054

TABLE II. (*Continued.*)

Transition J_{K_a,K_c} (upper←lower)	$H_2{}^{13}CCC$ Frequencies (MHz) Measured	O−C	$H_2C^{13}CC$ Frequencies (MHz) Measured	O−C	$H_2CC^{13}C$ Frequencies (MHz) Measured	O−C
$18_{3,16}\leftarrow 17_{3,15}$	···		···		359 869.720(30)	0.046
$18_{3,15}\leftarrow 17_{3,14}$	···		···		359.872.706(20)	−0.023
$18_{1,17}\leftarrow 17_{1,16}$	···		···		363 090.630(15)	0.011
$19_{0,19}\leftarrow 18_{0,18}$	383 181.983[b]		···		···	
$19_{2,18}\leftarrow 18_{2,17}$	383 446.162(20)	0.069	···		···	
$19_{3,17}\leftarrow 18_{3,16}$	383 463.994(15)	0.033	···		···	
$19_{3,16}\leftarrow 18_{3,15}$	383 468.182(15)	−0.041	···		···	
$19_{2,17}\leftarrow 18_{2,16}$	383 845.304(20)	0.061	···		···	
$19_{1,18}\leftarrow 18_{1,17}$	386 906.725(15)	−0.018	···		···	

Note: Calculated frequencies are derived from the constants in Table III.
[a]Due to significant but not accurately measureable splittings of the $K_a=3$ doublets at lower frequencies, these blended lines were entered into the fit as two lines with the centroid at the measured frequency and the splitting set to a value calculated from other lines.
[b]Not included in fit because accurate frequencies are unobtainable.

IV. DETERMINATION OF H_2CCC STRUCTURE

Various approaches have been used to obtain the best estimate of the equilibrium (r_e) structure—that derived most readily from *ab initio* calculations—from isotopic substitution. The mass dependent (r_m) structure[13] best approximates the r_e structure, but for molecules with more than two or three atoms, calculation of the r_m structure requires rotational constants from an excessively large number of isotopic species. In addition, for molecules containing hydrogen, the fractional change in atomic mass during deuterium substitution is so large that the perturbation approximation inherent in the r_m method tends to break down. More recently, an *ad hoc* empirical approach based on scaling the ground state moments of inertia was developed.[14,15] This method does not require an unreasonable amount of data, and produces results which approximate the r_e structure about as well as the r_m method; it suffers from complications similar to those of the r_m method when the molecule contains hydrogen. With this *ad hoc* method one can obtain accurate results with molecules containing hydrogen if vibrational frequencies are known.[16] Lacking that, however, this method apparently yields structures which are no more accurate than substitution (r_s) structures[6] determined from Kraitchman's equations.[5] Costain[6] demonstrated that zero-point vibrational effects cancel significantly when the position of each

TABLE III. Spectroscopic constants of H_2CCC isotopic species (in MHz).

Constant[a]	H_2CCC[b]	D_2CCC	$H_2{}^{13}CCC$	$H_2C^{13}CC$	$H_2CC^{13}C$
Rotational constants					
A	288 783 ± 34	145 155.2 ± 2.4	288 880 ± 120	288 610 ± 130	288 860 ± 130
B	10 588.639 ± 0.002	9 402.840 ± 0.005	10 278.637 ± 0.007	10 584.699 ± 0.005	10 180.316 ± 0.006
C	10 203.966 ± 0.002	8 818.135 ± 0.004	9 915.827 ± 0.006	10 200.497 ± 0.005	9 824.222 ± 0.007
Quartic centrifugal distortion constants					
$D_J\times10^3$	4.248 ± 0.002	3.128 ± 0.002	4.027 ± 0.005	4.240 ± 0.004	3.955 ± 0.005
D_{JK}	0.5164 ± 0.0005	0.3699 ± 0.0004	0.485 ± 0.002	0.518 ± 0.002	0.4850 ± 0.0022
D_K	23.535[c]	5.391[d]	23.535[c]	23.535[c]	23.535[c]
$d_1\times10^3$	−0.153 ± 0.002	−0.251 ± 0.003	−0.135 ± 0.006	−0.147 ± 0.004	−0.127 ± 0.005
$d_2\times10^3$	−0.070 ± 0.001	−0.1346 ± 0.0007	−0.058 ± 0.003	−0.078 ± 0.004	−0.063 ± 0.004
Sextic centrifugal distortion constants					
$H_{JK}\times10^6$	7.6 ± 0.2	5.5 ± 0.1	7.5 ± 0.7	13.3 ± 0.9	9.4 ± 0.5
$H_{KJ}\times10^3$	−1.28 ± 0.07	−0.34 ± 0.03	−1.5 ± 0.3	−0.80 ± 0.26	−1.43 ± 0.32
Octic centrifugal distortion constant					
$L_{KJ}\times10^3$	0.060 ± 0.003	0.0054 ± 0.0009	0.043 ± 0.012	0.092 ± 0.010	0.050 ± 0.012

[a]Rotational and centrifugal distortion constants for Watson's S-reduced Hamiltonian in the I^r representation (Ref. 9) from least-squares fit to data in Tables I and II, except H_2CCC (see Ref. 1). Uncertainties are 1σ.
[b]Constants from Ref. 1.
[c]Constrained to value for H_2CCO (Ref. 10) because of high correlation with A.
[d]Constrained to value for D_2CCO (Ref. 11) because of high correlation with A.

TABLE IV. Watson's determinable constants of H_2CCC isotopic species (in MHz).[a]

	A	*B*	*C*
H_2CCC	288 783(34)	10 589.163(2)	10 204.491(2)
$H_2{}^{13}CCC$	288 880(120)	10 279.130(7)	9 916.320(6)
$H_2C^{13}CC$	288 610(130)	10 585.225(5)	10 201.023(5)
$H_2CC^{13}C$	288 860(130)	10 180.808(6)	9 824.715(7)
D_2CCC	145 155(2)	9 403.215(5)	8 818.511(4)

[a]Uncertainties in parentheses are one standard deviation in units of the last quoted decimal place.

atom is determined by isotopic substitution at that position, an important consideration when determining the position of light atoms such as hydrogen.

The r_0 and r_s structures were determined here for H_2CCC because they could be derived directly from the experimental moments of inertia in Table V and because they approximate the r_e structure surprisingly well in ketene and formaldehyde. The next member in the cumulene carbene series, H_2CCCC, has also been detected in our laboratory[17] and a search for higher members in the series is underway. However, it may not be feasible to derive r_e structures for H_2C_5 and still larger cumulene carbenes by the method described in Sec. IV C. We therefore examined whether significant discrepancies are present in the r_0 and r_s structures for H_2CCC and made the same comparison in ketene—a very useful analog.

A. The r_0 structure

The r_0 structure of H_2CCC, summarized in Table IX, was obtained by least-squares fitting Kraitchman's equations[5] to the moments of inertia of four of the five species in Table V on the assumption that the molecule is planar. Because the middle C atom is only ~0.1 Å from the center of mass, the $H_2C^{13}CC$ moments were not used in the fit. If the r_0 structure of ketene is determined as here, the C=C bond is within 0.001 Å, the C=O bond within 0.003 Å, the C–H bond within 0.007 Å, and the HCH angle within 0.5° of those in the r_e structure[18] (r_e=1.0781 Å, α_e=122.36°, R_{1e}=1.3131 Å, and R_{2e}=1.1606 Å). In formaldehyde, the C=O bond length in the r_0 structure is nearly as close (i.e., within 0.005 Å) to the r_e distance[19] as in ketene, while the C–H bond and HCH angle are similarly discrepant. The surprisingly small differences between the C=C and C=O bond lengths in the r_0 and r_e structures of ketene and formaldehyde implied that the C=C bond lengths in the r_0 structure of H_2CCC may be within 0.005 Å of those of the r_e structure.

TABLE V. Moments of inertia and inertial defects of H_2CCC isotopic species (in uÅ^2).[a]

	I_a	I_b	I_c	Δ
H_2CCC	1.750 02(21)	47.725 774(9)	49.524 861(10)	0.049 07(21)
$H_2{}^{13}CCC$	1.749 43(73)	49.165 250(33)	50.964 067(31)	0.049 39(73)
$H_2C^{13}CC$	1.751 07(79)	47.743 529(23)	49.541 698(24)	0.047 10(79)
$H_2CC^{13}C$	1.749 55(79)	49.640 068(29)	51.439 253(37)	0.049 64(79)
D_2CCC	3.481 63(5)	53.745 022(29)	57.308 541(26)	0.081 89(6)

[a]Moments of inertia calculated from Watson's determinable constants (Table IV) taking $B\times I$=505 376 MHz uÅ^2. Uncertainties in parentheses are one standard deviation in units of the last quoted decimal place.

B. The r_s structure

On the assumption of C_{2v} symmetry, a full substitution structure could, in principle, be obtained for H_2CCC because isotopic substitutions were made at each atom. However, because the middle carbon is close to the center of mass, its position was determined by the first moment equation. This equation, while not yielding a position as accurately as a substitution of an atom far from the center of mass, is usually accurate to a few thousandths of an Å when locating the position of a C atom.[6] Owing to their light mass and thus large vibrational contribution to the rotational constants and inertial defect, it is usually difficult to locate hydrogen atoms precisely (see Ref. 20). However, in ketene the C–H bond is within 0.004 Å, the C=C bond within 0.003 Å, the C=O bond within 0.001 Å, and the HCH angle within 0.1° of the r_e structure; similarly, in formaldehyde the bond lengths are within 0.003 Å and the bond angle within 0.2° of the r_e structure. Therefore, by analogy with ketene and formaldehyde, it was anticipated that the r_s structure of H_2CCC in Table IX, derived from the pair (I_a, I_b), should closely approximate the equilibrium geometry.

C. The r_e structure

For a molecule the size of H_2CCC the determination of an accurate equilibrium structure solely on the basis of experimental data is a formidable problem in principle, and quite impossible for H_2CCC with the information available. Even if a large number of rotational constants in many different vibrational states were available for several isotopic species, perturbations between vibrational states, which are quite common in polyatomic molecules, are a serious potential source of systematic error. On the other hand, the *ab initio* determination of bond lengths to an accuracy of 0.001 Å or better and of bond angles to better than 0.3° is a difficult task for a molecule with four independent geometric parameters and 20 electrons. Such a determination might be feasible with methods like the coupled cluster approximation including single and double excitations with perturbative treatment of connected triple excitations [CCSD(T); Ref. 21] but, for accurate results, that might require basis sets of the order of 200 contracted Gaussian-type orbitals, and would require all electrons to be correlated. A simpler alternative, applicable also to larger problems, consists in the combination of experimental and theoretical data. This approach has been adopted for several linear molecules with 3–5 atoms.[22–26] Highly accurate ground state rotational constants B_0 (and A_0 and C_0 where this applies) are taken from experiment, and the differences $\Delta B_0 = B_e - B_0$ are then calculated. This may be done either variationally or by means of perturbation theory. While the variational method is more accurate, perturbation theory is much easier to apply and, for semirigid molecules, usually leads to very similar results. Since the

TABLE VI. CEPA-1 quadratic force constants for H_2CCC.

Force constant[a]	Value	Force constant	Value
F_{11}	0.359 377 4	F_{55}	0.065 446 0
F_{22}	0.107 214 6	F_{66}	0.015 975 4
F_{33}	0.607 998 4	F_{56}	0.003 067 5
F_{44}	0.659 522 8	F_{77}	0.354 688 0
F_{12}	−0.010 727 9	F_{88}	0.121 821 0
F_{13}	0.012 918 5	F_{99}	0.048 837 6
F_{14}	−0.000 525 1	F_{78}	−0.016 437 0
F_{23}	0.029 491 4	F_{79}	0.001 290 0
F_{24}	0.002 201 2	F_{89}	−0.011 428 2
F_{34}	0.015 613 3		

[a]Defined as $F_{ij}=(\partial^2 V/\partial S_i\,\partial S_j)_e$, in atomic units.

variational calculation of rovibrational states is a formidable problem for a penta-atomic molecule we have made use of standard second-order perturbation theory in normal-coordinate space (see, e.g., Refs. 19 and 27) in order to calculate the differences between equilibrium and ground state rotational constants

$$\Delta B_0 = B_e - B_0 \approx \sum_r \alpha_r^B/2. \tag{1}$$

In the case of an asymmetric top, analogous equations apply for ΔA_0 and ΔC_0.

The calculation of the vibration–rotation coupling constants (α_r^A, α_r^B, and α_r^C) requires knowledge of the cubic force field. We have calculated this field by means of Meyer's coupled electron pair approximation[28] (CEPA) making use of a basis set of 131 contracted Gaussian-type orbital (cGTOs): 11*s*, 6*p*, 2*d*, 1*f*/6*s*, 2*p* in contraction [8,4,2,1/4,2] where exponents of the *s* and *p* functions for carbon and the *s* functions for hydrogen are taken from Huzinaga.[29] The carbon *d* exponents are chosen to be 1.2 and 0.4, the *f* exponent is 0.8, and the hydrogen *p* exponents are 1.2 and 0.3. All valence electrons were correlated in the CEPA calculations which were mainly carried out with the MOLPRO92 suite of programs[30] on an IBM workstation RISC/6000 model 320H. Version 1 of CEPA was used and canonical molecular orbitals were employed. The CEPA-1 equilibrium geometry is $r_e=1.0852$ Å, $\alpha_e(\widehat{HCH})=117.39°$, $R_{1e}=1.3263$ Å, and $R_{2e}=1.2919$ Å; the corresponding total energy is −115.104 836 a.u.

The cubic force field of H_2CCC is defined in terms of symmetry coordinates S_i which are identical to those used by Duncan *et al.*[31] for H_2CCO, with the exception of a different normalization employed for the symmetric CH_2 bending coordinate and a slightly different numbering. S_1 to S_4 are totally symmetric coordinates described as symmetric CH stretch, symmetric CH_2 bend [defined as $S_2=(1/\sqrt{6})(\Delta\beta_1+\Delta\beta_2-2\Delta\alpha)$], $C_{(1)}C_{(2)}$ stretch [employing the atomic numbering scheme $H_2C_{(1)}C_{(2)}C_{(3)}$] and $C_{(2)}C_{(3)}$ stretch, respectively. S_5 and S_6, of B_1 symmetry, describe out-of-plane bending motions, with the latter referring to $C_{(1)}C_{(2)}C_{(3)}$ bending. The remaining symmetry coordinates S_7 to S_9 belong to symmetry species B_2 and correspond to antisymmetric CH stretch, antisymmetric CH bend and in-plane $C_{(1)}C_{(2)}C_{(3)}$ bend.

The harmonic vibrational frequencies (in cm^{-1}) calculated from the quadratic force constants in Table VI are $\omega_1(a_1)=3137.5$, $\omega_2(a_1)=2009.6$, $\omega_3(a_1)=1495.9$, $\omega_4(a_1)=1133.4$, $\omega_5(b_1)=1014.1$, $\omega_6(b_1)=175.7$, $\omega_7(b_2)=3249.8$, $\omega_8(b_2)=1003.8$, and $\omega_9(b_2)=294.4$. These frequencies are in reasonable agreement with the previous MP2/6–31G* results of Maier *et al.*[32] A more detailed discussion of our theoretical results for the positions and intensities of vibrational bands of H_2CCC isotopic species in comparison with matrix IR data will be given elsewhere.[33]

According to experience in Göttingen with about 100 other molecules most of the calculated diagonal force constants have probable errors of ~2%. A larger relative error for H_2CCC is expected for F_{66}, the out-of-plane CCC bending force constant, because it is strongly influenced by basis set and correlation effects. In particular, the influence of *f* functions is very pronounced: their presence increases F_{66} from 0.002 298 a.u. or 0.010 019 aJ to 0.015 975 a.u. or 0.069 649 aJ. The latter value is probably still too low. CCSD(T) calculations with a smaller basis set of 108 cGTOs (Dunning's[34] cc-VTZ basis set exclusive of *d* functions at the hydrogen nuclei) again carried out with MOLPRO92,[30,35,36] yield an increase in F_{66} by 36.2% relative to a CEPA-1 calculation with the same basis set. We therefore recommend a value of $F_{66}=0.02176$ a.u., obtained by scaling the CEPA-1/131 cGTO value with a factor of 1.362. It may still have an uncertainty of ~10%. Together with the other quadratic force constants from the CEPA-1 calculations this yields $\omega_6=205$ cm^{-1}. This value is not at variance with the matrix IR experiments of Reisenauer[37] who found no noticeable absorption attributable to ν_6 (H_2CCC) above 220 cm^{-1}.

From the quadratic force field, the equilibrium quartic centrifugal distortion constants of H_2CCC are calculated to be $D_J^{(e)}=3.76$ kHz, $D_{JK}^{(e)}=0.421$ MHz, $D_K^{(e)}=21.948$ MHz, $d_1^{(e)}=-0.143$ kHz, and $d_2^{(e)}=-0.039$ kHz. Similar calculations for H_2CCO yielded $D_K^{(e)}=20.567$ MHz, to be compared with an experimental ground state value[10] of 23.535 MHz. A rather accurate estimate of the ground state D_K value of H_2CCC should be possible by scaling the theoretical $D_K^{(e)}$ value with a factor of 1.144 which corresponds to the ratio $D_K(\text{exp.})/D_K^{(e)}$ for H_2CCO. The result is D_K (H_2CCC) = 25.1 MHz. This may be somewhat too low since H_2CCC, owing to the rather shallow CCC out-of-plane bending potential, is more floppy than H_2CCO. In a similar way, D_K (D_2CCC) is predicted to be 6.09 MHz. On the whole, the present *ab initio* calculations support the validity of the approximation of assuming equal D_K values for H_2CCC and H_2CCO isotopic species.

The CEPA-1 cubic force constants in Table VII, defined as $F_{ijk}=(\partial^3 V/\partial S_i\,\partial S_j\,\partial S_k)_e$, were numerically transformed into normal-coordinate space allowing the vibration–rotation coupling constants to be calculated via the formula (see, e.g., Ref. 38)

TABLE VII. CEPA-1 cubic force constants for H_2CCC (in a.u.).

Force constant	Value	Force constant	Value
F_{111}	−0.766 491 6	F_{256}	0.002 632 3
F_{222}	0.044 152 2	F_{266}	−0.001 010 6
F_{333}	−1.807 621 8	F_{277}	−0.020 958 2
F_{444}	−2.146 235 4	F_{278}	0.003 302 3
F_{112}	0.010 899 8	F_{279}	−0.025 109 3
F_{113}	0.007 948 4	F_{288}	−0.058 579 8
F_{114}	0.000 697 2	F_{289}	0.021 197 6
F_{122}	−0.027 943 8	F_{299}	0.036 366 8
F_{123}	−0.007 782 1	F_{334}	−0.034 617 2
F_{124}	−0.000 768 3	F_{344}	0.011 613 6
F_{133}	−0.021 507 0	F_{355}	−0.051 264 4
F_{134}	0.002 181 3	F_{356}	−0.025 684 7
F_{144}	−0.004 048 8	F_{366}	0.018 226 2
F_{155}	−0.026 147 0	F_{377}	0.016 640 0
F_{156}	−0.006 611 0	F_{378}	0.027 227 0
F_{166}	0.003 342 6	F_{379}	−0.005 963 7
F_{177}	−0.818 659 8	F_{388}	−0.028 783 6
F_{178}	0.010 630 9	F_{389}	0.005 125 4
F_{179}	0.007 700 6	F_{399}	−0.068 492 4
F_{188}	−0.031 495 4	F_{455}	0.021 430 2
F_{189}	−0.018 593 8	F_{456}	−0.023 478 6
F_{199}	−0.078 441 2	F_{466}	0.189 247 2
F_{223}	−0.012 347 6	F_{477}	0.046 080 0
F_{224}	−0.005 715 2	F_{478}	0.017 968 0
F_{233}	−0.006 444 0	F_{479}	−0.023 076 9
F_{234}	0.002 532 7	F_{488}	0.002 101 0
F_{244}	0.007 919 8	F_{489}	0.026 221 4
F_{255}	0.012 077 2	F_{499}	−0.031 725 0

$$-\alpha_r^B=\frac{2B_e^2}{\omega_r}\left[\sum_{\xi}\frac{3(a_r^{(b\xi)})^2}{4I_\xi^{(e)}}+\sum_{s\neq r}(\zeta_{r,s}^{(b)})^2\frac{(3\omega_r^2+\omega_s^2)}{\omega_r^2-\omega_s^2}+\pi\left(\frac{c}{h}\right)^{1/2}\sum_s\phi_{rrs}\,a_s^{(bb)}\left(\frac{\omega_r}{\omega_s^{3/2}}\right)\right]. \quad (2)$$

Analogous formulas hold for α_r^A and α_r^C. The results are given in Table VIII.

Strong Coriolis interactions are to be expected between the ν_5 and ν_8 bands, which correspond to the CH_2 wagging and CH_2 rocking vibrations, and between the CCC out-of-plane (ν_6) and in-plane (ν_9) bending vibrations. The corresponding Coriolis coupling constants are calculated to be $|\zeta_{5,8}^{(a)}|=0.4820$ and $|\zeta_{6,9}^{(a)}|=0.9593$. Second-order perturbation theory is not adequate to calculate reliable values for the vibration–rotation coupling constants of these interacting states. Although the large Coriolis contributions [second term in Eq. (2)] cancel almost completely upon forming the sum over α_r^A values, and the usual way to remove the terms with small resonance denominators (see, e.g., Refs. 19 and 27) leads exactly to the same ΔA_0 values, we are not convinced that the present ΔA_0 values are very reliable. Therefore, we have used only $I_b^{(e)}$ and $I_c^{(e)}$ values in the determination of the equilibrium geometry. Least-squares fit to ten such data yields the following values for the geometrical parameters: $r_e=1.084\,72$ Å, $\alpha_e=117.853°$, $R_{1e}=1.328\,63$ Å, and $R_{2e}=1.292\,04$ Å. This structure reproduces all input B_e's and C_e's with a maximum deviation of 1.2 MHz.

Recalculating the vibration–rotation coupling constants with a modified cubic force field which involves the recommended value for F_{66}, and carrying out the same kind of least-squares fit as described above, we find that $r_e=1.082\,76$ Å, $\alpha_e=117.643°$, $R_{1e}=1.328\,34$ Å, and $R_{2e}=1.291\,03$ Å. This is currently our best estimate of the equilibrium geometry of propadienylidene (Fig. 1). The R_{1e} value should be accurate to 0.0005 Å. R_{2e} and r_e may have errors of ~0.001 Å and the uncertainty in α_e should not exceed 0.2°.

The electric dipole moment of H_2CCC has been calculated at the recommended equilibrium geometry by different methods, all making use of the 131 cGTO basis set. The moments are (in D) −4.305 (SCF), −4.435 (MP2), −4.052 (CEPA-1), −4.089 (CCSD), and −4.135 [CCSD(T)]. The last value is expected to be the most reliable one; it should be accurate to about 0.03 D.

TABLE VIII. Calculated vibration–rotation coupling constants (in MHz) for H_2CCC (CEPA-1/131 cGTO).[a,b]

No. of mode (i)	α_i^A	α_i^B	α_i^C
1	4788	6.7	12.8
2	247.4	77.9	73.2
3	−2967	−17.7	11.9
4	159.5	25.2	20.4
5	−252 038(4281)	12.0	−14.6
6	98 200(4197)	−116.7	−149.6
7	3 154	6.3	7.0
8	251 196(−5122)	−16.2	10.0
9	−92 825(1178)	−67.5	−32.1

[a]Values for further isotopic species are available upon request. Deperturbed values (see Refs. 19 and 27) are given in parentheses.

[b]Making use of the recommended F_{66} value (see the text) changes α_6^B and α_6^C to −98.6 and −127.3 MHz, respectively, with the other α_i^B and α_i^C values remaining unchanged. The changes in the α_i^A values (of no relevance to the present determination of the equilibrium geometry) are available from the authors upon request.

TABLE IX. H_2CCC structures.

Structures	$r(H–C_{(1)})$ Å	$r(C_{(1)}–C_{(2)})$ Å	$r(C_{(2)}–C_{(3)})$ Å	$\angle(HC_{(1)}H)$ (deg)
Measured				
r_0	1.098±0.007	1.324±0.003	1.291±0.003	118.8±0.5
r_s	1.084±0.004	1.326±0.003	1.287±0.003	117.7±0.2
Recommended structure (theory plus experiment)				
r_e	1.083±0.001	1.3283±0.0005	1.291±0.001	117.6±0.2
Theory[a]				
r_e	1.085	1.326	1.292	117.4

[a]CEPA-1/131 cGTO (valence electrons correlated).

V. CONCLUSION

The structure of H_2CCC, a molecule unknown in the gas phase 2 years ago, has been determined by isotopic substitution to an accuracy comparable to that with which the structure of the stable molecule ketene, H_2CCO, is known. The vibration–rotation coupling constants required to determine the equilibrium geometry of H_2CCC from the experimental data have been derived from an *ab*

initio calculation of the vibrational structure of H_2CCC. The equilibrium values for the three bond lengths and the HCH angle are in very satisfactory agreement with theory, the angle agreeing to within 0.2°, and the bonds to within 0.2%. The r_s structure (Table IX) is remarkably close to the equilibrium geometry. In the absence of a suitable *ab initio* calculation, the r_s structure may provide a good estimate of the equilibrium geometry of higher members in the cumulene carbene series.

Note added in proof. The equilibrium geometry of H_2CCC was also calculated by CCSD(T) using the 108 cGTO basis described in the text and correlating all electrons. The result is $r_e=1.0815$ Å, $\alpha_e=117.35°$, $R_{1e}=1.3277$ Å, and $R_{2e}=1.2893$ Å. The corresponding total energy is $V_e=-115.157\,855$ a.u. According to our experience with this method and basis set it tends to underestimate CH equilibrium bond lengths by 0.001 to 0.002 Å. These calculations are thus in support of our recommended r_e value of 1.0828 Å. The CCSD(T) harmonic vibrational frequencies for totally symmetric vibrations are (in cm^{-1}): $\omega_1=3139$, $\omega_2=2020$, $\omega_3=1489$, and $\omega_4=1124$. They differ from the CEPA-1 values by no more than 10 cm^{-1}.

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