Microwave spectroscopic detection of HCCP in the X 3 Σ − electronic state: Phospho-carbene, phospho-allene, or phosphorene?

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Microwave spectroscopic detection of HCCP in the $X\,^3\Sigma^-$ electronic state: Phospho-carbene, phospho-allene, or phosphorene?

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Microwave spectrum of the HCCP radical was detected for the first time in the $X\,^3\Sigma^-$ ground electronic state using a source-modulated microwave spectrometer. In total, 24 rotational transitions of HCCP in the 90–360 GHz region, 9 rotational transitions of DCCP in the 260–360 GHz range, and 24 rotational transitions of $H^{13}C^{13}CP$ between 130–360 GHz were measured. Hyperfine structure pertaining to the phosphorus and hydrogen nuclei was observed for HCCP, and in the case of $H^{13}C^{13}CP$, only for phosphorus. The corresponding hyperfine coupling constants were ascertained in addition to the rotational, centrifugal distortion, and fine structure constants by a least-squares analysis of the measured frequencies. From the hyperfine coupling constants determined, the spin density of unpaired electrons was estimated to be 76% for the phosphorus atom and 42% for the carbon adjacent to the hydrogen. The r_0 structure of HCCP was established from the rotational constants of HCCP and its isotopically substituted species: $r_0(CP) = 1.685$ Å, $r_0(CC) = 1.241$ Å, and $r_0(CH) = 1.057$ Å. These structural features are consistent with a linear phospho-allenic form that has been somewhat modified by a phosphorene. © *1997 American Institute of Physics.* [S0021-9606(97)02029-1]

INTRODUCTION

Phosphorus-bearing molecules such as phosphoric acid are well known. Such molecules have attracted much attention in the field of chemistry because the phosphorus atom shows more metaphoric compounds than the isovalent nitrogen atom. Phosphoric acid is even known to have various forms such as H_3PO_4, H_3PO_3, H_3PO_2, H_2PO_3, HPO_2, HPO_3, $H_4P_2O_5$, $H_4P_2O_7$, etc. Reaction intermediates resulting in these hydroxyphosphorus compounds have been well studied and characterized in recent years by microwave spectroscopy: PH,[1] PH2,[2] PO,[3] PO2,[4] HPO,[5] and H2PO.[6]

In contrast to these hydroxyphosphorus compounds, CP bond-bearing molecules are relatively unknown in the laboratory, except for large complex molecules. However, there is a great deal of interest in simple phosphorus-bearing organic compounds because of increasing detection of carbon-chain-bearing interstellar molecules, most of which are mainly generated in space by ion–molecule reactions.[7] The first and sole CP bond-bearing species detected in space[8] is the CP radical, spectral lines of which were identified in the envelope of a carbon star on the basis of line frequencies measured in the laboratory.[9] This detection as well as that of the first phosphorus-containing interstellar molecule, PN,[10,11] have stimulated studies and discussions on phosphorus chemistry in interstellar space.[12–15] Millar and his collaborators predicted that phosphorus-bearing carbon-chain molecules such as CCP and HCCP may exist in the molecular hot core of star-forming regions with higher abundances than that of CP, if no oxygen is injected into the gas phase from dust grains.[14,15] However, astronomical observations of these phosphorus-bearing molecules have not been carried out because no accurate frequencies of their spectral lines are known by laboratory spectroscopy. Only a few *ab initio* studies have been carried out on CCP[16] and C3P.[17] No quantum chemical calculations have been reported on the phosphorus-bearing radical, HCCP.

The isovalent nitrogen-containing carbene radical, HCCN, has been well characterized by microwave spectroscopy. Saito *et al.*[18] detected fine structure rotational spectral lines of HCCN in the millimeter-wave region and showed that the observed spectral lines were well explained by a Hamiltonian of a linear molecule in the $^3\Sigma^-$ electronic state. However, Rice and Schaeffer[19] carried out a high-level *ab initio* calculation on HCCN in a MCSCF-CISD level with DZP and TZ2P bases, which predicted a bent structure for HCCN in the ground electronic state. Brown *et al.*[20] determined the r_s structure of HCCN by measuring spectral lines of its isotopic species and suggested that HCCN may have a quasilinear conformation of the carbene frame. Many experimental[21–25] and theoretical[26] studies have been devoted to the troublesome issue of the geometry of HCCN: does it have a cyanocarbene or allenic structure? Endo *et al.*[21] observed two components of the lowest rotational transition by using Fourier transform microwave spectroscopy, and on the basis of the hyperfine coupling constants obtained for the nitrogen and hydrogen nuclei they suggested that HCCN has an almost linear form with a possibility of a large-amplitude bending motion, as proposed by Brown *et al.*[20] McCarthy *et al.*[23] studied HCCN and DCCN in the vibrationally excited states of their bending modes, and concluded that HCCN is a quasilinear molecule with a much lower CCH bending mode.

In this paper we present the first detection of a phosphorus-bearing radical, HCCP, by microwave spectroscopy. The r_0 structure was determined and the spin densities on the phosphorus and carbon atoms were derived in order to clarify the structural feature of HCCP in the ground electronic state.

EXPERIMENTAL DETAILS

A source-modulated microwave spectrometer covering the range up to 620 GHz was employed in conjunction with a 2 m free space cell at the Institute for Molecular Science.[27] Outputs of frequency multipliers driven by millimeter-wave klystrons were used as higher millimeter- and submillimeter-wave sources.

Premixed phosphine and acetylene gas was dc discharged in the aforementioned cell and new paramagnetic lines, which showed a large Zeeman effect by application of about 30 G magnetic field were searched for in the relatively high-sensitivity frequency region of 360 GHz with the aim of detecting phosphorus-bearing carbon-chain radicals such as CCP, C_3P, or HCCP. This discharge system also generated intense lines from the PH_2 radical in the frequency region of the observations. Such lines were conveniently eliminated from the observed lines on comparison with their corresponding cited literature frequencies.[28,29] Other diamagnetic lines were distinguished from lines of interest, all of which showed paramagnetic behavior. Thus, all known lines from possible species generated in the same experimental system were excluded from the observed lines.

Several paramagnetic lines whose generation required both phosphine and acetylene remained unidentified in the frequency region of 360 GHz. Among them there were two distinct and strong lines at 359 558 and 359 779 MHz with nearly equal intensity and immediately a line with similar intensity showing a relatively small Zeeman effect was found at 359 679 MHz, between the former two lines. A possible free radical for these triplet lines was suspected to be HCCP in the $^3\Sigma^-$ state. This assumption proved to be correct as other triplet lines were observed in the 348 GHz region. Paramagnetic lines believed to be due to HCCP were verified by testing their chemistry while simultaneously viewing a line on the oscilloscope at a given frequency. Each of the constituent gases was, in turn, reduced gradually to zero partial pressure and the resultant effect observed. Unknown lines were treated in the same fashion as for confirmed HCCP lines and hence appropriately included or eliminated. Having proved which lines originated from HCCP, the effect of altering the partial pressures of each of the gases involved and the experimental conditions on one of the lines was examined in order to establish the precise optimum conditions. The triplet line series showed hyperfine structures, first due to the phosphorus nucleus for lower-N rotational transitions starting from $N=21-20$ and then due to the hydrogen nucleus for the lowest three rotational transitions observed. These observations have definitely established the identification of HCCP in the gas phase.

Optimum conditions for the production of HCCP were partial pressures of 17 mTorr of PH_3 and 6 mTorr of C_2H_2. DCCP and $H^{13}C^{13}CP$ radicals were formed in a similar fashion, but by premixing phosphine and deuterated acetylene in the case of DCCP and PH_3 and $^{13}C_2H_2$ in the case of $H^{13}C^{13}CP$. Throughout the experiments the discharge current was set to 100 mA and the temperature of the cell was maintained at around -100 °C by adjusting the flow of liquid
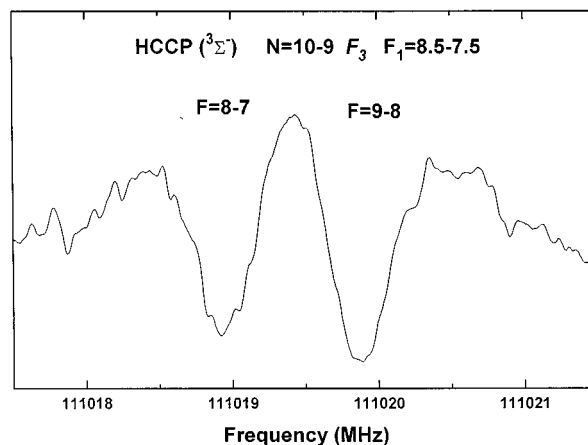

FIG. 1. Hyperfine structure due to the H nucleus, $F_1=8.5-7.5$ of the $N=10-9$, F_3 transition of HCCP, observed by dc-glow discharge (100 mA) in a mixture of PH_3 (17 mTorr) and C_2H_2 (6 mTorr) in the free space cell maintained at -100 °C. The integration time was 120 s.

nitrogen around a copper jacket attached to the cell. Using helium gas in combination with the discharged mixture had no effect on the resulting spectra. In order to assign the spectral lines of the isotopic species, preliminary constants for each isotopic species were derived by using the molecular parameters of HCCN, with the exception of the CP bond length, which was assumed to be the CP bond length of HCP, 1.5421 Å,[30] and were used to predict the line frequencies of the isotopic species.

For HCCP, 98 spectral lines for 24 rotational transitions ranging from $N=8-7$ to $N=32-31$ were measured over the 90–360 GHz region. F_3 components of the $N=11-10$ to 9–8 transitions and the F_1 component of the $N=8-7$ transition appeared as resolved hyperfine structures due to the hydrogen nucleus, as demonstrated in Fig. 1 for one of the F_3 components of the $N=10-9$ transition, though most of the measured lines were found to be overlapped with each other. A much stronger unresolved line at high frequency, the F_1 component of the $N=32-31$ transition, is shown in
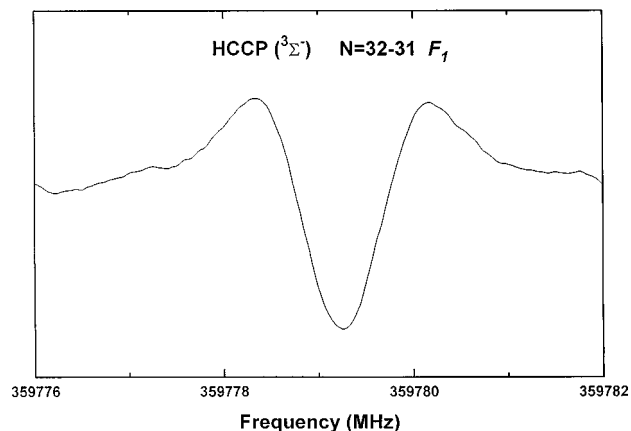

FIG. 2. The F_1 component of the $N=32-31$ transition of HCCP observed under similar experimental conditions as these given in the caption of Fig. 1. The integration time was 8 s.

TABLE I. Observed and calculated transition frequencies of the HCCP ($^3\Sigma^-$) radical (MHz).[a]

$N'-N''$	$F_1\ \nu_{obs}(\Delta\nu)$[b]	$F_2\ \nu_{obs}(\Delta\nu)$[b]	$F_3\ \nu_{obs}(\Delta\nu)$[b]
8–7	91 408.479 (−0.016)[c]	89 967.908 (0.017)[d]	
	91 401.704 (0.062)[c]	89 965.738 (−0.015)[d]	
	91 402.483 (0.045)[c]		
9–8		101 212.648 (0.013)[d]	99 466.262 (−0.118)[c,f]
			99 465.152 (0.002)[c]
		101 210.939 (−0.013)[d]	99 471.859 (0.012)[c]
10–9	113 476.007 (0.005)[d]	112 457.107 (0.009)[d]	111 014.878 (−0.010)[c]
			111 013.905 (−0.035)[c]
		112 455.726 (−0.012)[d]	111 020.058 (−0.001)[c]
			111 019.108 (−0.008)[c]
11–10	124 571.631 (−0.014)[d]	123 701.223 (−0.002)[d]	122 499.137 (0.014)[c]
12–11	124 568.188 (0.039)[d]	123 700.089 (−0.014)[d]	122 498.399 (0.013)[c]
	135 695.323 (0.015)[d]	134 945.008 (0.039)[d]	133 924.376 (−0.082)[d,e]
	135 692.458 (0.015)[d]	134 944.025 (−0.003)[d]	133 927.448 (0.205)[d,f]
13–12	146 840.318 (−0.043)[d]	146 188.275 (−0.013)[d]	145 316.215 (−0.032)[d]
	146 837.968 (−0.016)[d]	146 187.475 (−0.012)[d]	
14–13	158 001.881 (−0.036)[d]	157 431.167 (0.028)[d]	156 679.158 (0.011)[d]
	157 999.914 (−0.012)[d]	157 430.449 (0.003)[d]	156 681.251 (0.040)[d]
15–14	169 176.320 (−0.013)[d]	168 673.168 (−0.024)	168 019.715 (0.004)[d]
	169 174.624 (−0.024)[d]		168 021.434 (0.037)[d]
16–15	180 360.847 (−0.003)[d]	179 915.033 (0.009)	179 342.769 (0.022)[d]
	180 359.369 (−0.043)[d]		179 344.218 (0.081)[d,e]
18–17	202 752.149 (−0.058)[d]	202 396.866 (−0.014)	201 949.594 (−0.031)[d]
	202 751.072 (−0.064)[d]		201 950.678 (0.083)[d,e]
19–18	213 956.149 (0.030)[d]	213 636.841 (0.012)	
	213 955.146 (−0.038)[d]		
20–19	225 164.108 (0.042)[d]	224 876.120 (0.043)	224 519.461 (0.044)
	225 163.204 (−0.042)[d]		
21–20	236 375.242 (0.016)[d]	236 114.585 (−0.003)	235 793.841 (0.041)
	236 374.467(−0.035)[d]		
22–21	247 588.562 (−0.054)	247 352.309 (−0.014)	247 062.722 (0.039)
23–22	258 804.346 (−0.004)	258 589.269 (0.023)	258 326.821 (0.009)
24–23	270 021.625 (0.004)	269 825.315 (−0.006)	269 586.792 (0.012)
25–24		281 060.528 (0.017)	280 843.071 (0.011)
26–25	292 459.342 (0.028)	292 294.797 (0.019)	292 096.034 (0.001)
27–26	303 679.202 (0.060)	303 528.080 (−0.005)	303 346.001 (−0.002)
28–27	314 899.309 (0.072)[e]	314 760.379 (−0.018)	314 593.155 (−0.064)
29–28	326 119.594 (0.016)	325 991.672 (−0.003)	325 837.845 (−0.033)
30–29	337 339.817 (0.015)	337 221.871 (−0.012)	337 080.137 (−0.007)
31–30	348 559.870 (0.056)	348 450.985 (0.001)	348 320.095 (−0.051)
32–31	359 779.531 (0.059)	359 678.917 (−0.025)	359 557.948 (−0.041)

[a]The standard deviation of the fit is 30.7 kHz.

[b]$\Delta\nu = \nu_{obs} - \nu_{calc}$. ν_{calc} is obtained from the molecular constants in Table IV.

[c]Hyperfine splitting components due to both the P and H nuclei. The assignments are $(F=F_1+\frac{1}{2},\ F_1=J+\frac{1}{2})$, $(F=F_1-\frac{1}{2},\ F_1=J+\frac{1}{2})$, $(F=F_1+\frac{1}{2},\ F_1=J-\frac{1}{2})$, and $(F=F_1-\frac{1}{2},\ F_1=J-\frac{1}{2})$, for the first line to the fourth lines, respectively.

[d]Hyperfine splitting components due to the P nucleus. The assignments are $F_1=J+\frac{1}{2}$ and $F_1=J-\frac{1}{2}$, for the upper and lower lines, respectively. See the text for details about the coupling scheme.

[e]Line weighted to 0.1.

[f]Line weighted to 0.0.

Fig. 2 for comparison of the signal to noise ratios. For DCCP, 26 lines for nine rotational transitions from $N=26-25$ to $N=35-34$, with omission of $N=28-27$, were recorded over the 260–360 GHz region. 76 lines from 24 rotational transitions of H^{13}C^{13}CP were measured over the 130–380 GHz range, where the hyperfine structure due to the phosphorus nucleus was resolved for lower-N transitions starting from the $N=22-21$ transition. Lines originating from HCCP were found to be the most intense and lines from DCCP more so than from H^{13}C^{13}CP. Each line fre-

quency was determined by averaging five pairs of upward and downward frequency sweep measurements. The observed line frequencies are listed in Table I for HCCP, Table II for DCCP, and Table III for H^{13}C^{13}CP.

ANALYSIS

Since the ground electronic state of HCCP is thought to be $^3\Sigma^-$ and there are two nuclei with nonzero nuclear spin, the appropriate Hamiltonian used in the present analysis is as follows:

TABLE II. Observed and calculated transition frequencies of the DCCP radical (MHz).[a]

$N'-N''$	$F_1\ \nu_{obs}(\Delta\nu)$[b]	$F_2\ \nu_{obs}(\Delta\nu)$[b]	$F_3\ \nu_{obs}(\Delta\nu)$[b]
26–25	267 397.363 (0.036)	267 207.859 (−0.023)	266 981.238 (−0.030)
27–26	277 652.765 (0.048)	277 478.191 (0.014)	277 270.026 (0.044)
29–28	298 165.211 (−0.085)[c]	298 016.368 (−0.012)	297 839.492 (−0.004)
30–29	308 422.042 (−0.048)	308 284.224 (−0.008)	308 120.710 (−0.003)
31–30	318 678.922 (−0.076)[c]	318 551.224 (0.011)	
32–31	328 935.875 (−0.002)	328 817.308 (0.017)	328 676.845 (0.006)
33–32	339 192.593 (−0.007)	339 082.443 (0.003)	338 951.986 (0.010)
34–33	349 449.057 (0.001)	349 346.632 (0.002)	349 225.297 (0.015)
35–34	359 705.171 (0.032)	359 609.822 (−0.008)	359 496.786 (−0.038)

[a]The standard deviation of the fit is 26.3 kHz.
[b]$\Delta\nu=\nu_{obs}-\nu_{calc}$. ν_{calc} is obtained from the molecular constants in Table IV.
[c]Line weighted to 0.1.

TABLE III. Observed and calculated transition frequencies of the H^{13}C^{13}CP radical (MHz).[a]

$N'-N''$	$F_1\ \nu_{obs}(\Delta\nu)$[b]	$F_2\ \nu_{obs}(\Delta\nu)$[b]	$F_3\ \nu_{obs}(\Delta\nu)$[b]
12–11	130 288.248 (0.064)[c] 130 285.121 (0.046)[c]	129 502.352 (−0.025)[c]	
13–12	140 976.579 (−0.040)[c] 140 974.135 (0.100)[c,d]	140 293.426 (−0.052)[c] 140 292.515 (−0.031)[c]	
14–13	151 681.952 (−0.039)[c] 151 679.879 (0.058)[c]	151 082.635 (−0.035)	
15–14	162 400.606 (−0.012)[c] 162 398.866 (0.088)[c,e]	161 871.891 (0.056)	161 187.338 (−0.009)[c]
16–15	173 129.667 (−0.037)[c] 173 128.100 (−0.030)[c]	172 660.542 (−0.009)	172 061.722 (0.123)[c,d]
17–16		183 448.592 (0.009)	182 918.605 (−0.034)[c]
18–17	194 611.136 (0.010)[c] 194 609.906 (−0.043)[c]	194 236.144 (0.007)	
19–18	205 360.482 (0.010)[c] 205 359.409 (−0.034)[c]	205 023.063 (0.002)	
20–19	216 114.123 (0.038)[c] 216 113.143 (−0.038)[c]	215 809.373 (0.031)	215 432.824 (0.018)[c] 215 433.646 (0.099)[c,e]
21–20	226 871.130 (0.007)[c] 226 870.282 (−0.042)[c]	226 594.903 (−0.039)	226 256.202 (0.020)
22–21	237 630.911 (0.012)[c] 237 630.162 (−0.027)[c]	237 379.856 (0.024)	237 073.649 (0.065)
23–22	248 164.056 (0.081)[e]	247 886.139 (−0.007)	
24–23	259 156.209 (−0.027)	258 947.321 (−0.016)	258 694.506 (0.020)
25–24	269 921.111 (−0.135)[d]	269 729.907 (0.021)	269 499.048 (−0.046)
26–25	280 687.216 (−0.027)	280 511.594 (0.006)	280 300.407 (0.036)
27–26	291 453.962 (0.013)	291 292.440 (0.032)	291 098.618 (−0.017)
28–27	302 221.124 (0.004)	301 894.148 (−0.002)	
29–28	312 988.596 (0.045)	312 851.223 (−0.042)	312 687.170 (0.043)
30–29	323 756.057 (−0.002)	323 629.261 (0.025)	323 477.741 (0.005)
31–30	334 523.494 (0.009)	334 406.195 (0.006)	334 266.094 (−0.025)
32–31	345 290.663 (−0.023)	345 182.101 (0.010)	345 052.306 (−0.084)[e]
33–32	356 057.578 (0.041)	355 956.910 (0.002)	355 836.600 (−0.041)
34–33	366 823.951 (0.029)	366 730.598 (−0.007)	366 618.976 (0.029)
35–34	377 589.761 (0.022)	377 503.110 (−0.039)	377 399.303 (−0.061)

[a]The standard deviation of the fit is 32.7 kHz.
[b]$\Delta\nu=\nu_{obs}-\nu_{calc}$. ν_{calc} is obtained from the molecular constants in Table IV.
[c]Hyperfine splitting components due to the P nucleus. The assignments are $F_1=J+\frac{1}{2}$ and $F_1=J-\frac{1}{2}$, for the upper and lower lines, respectively. See the text for details about the coupling scheme.
[d]Line weighted to 0.0.
[e]Line weighted to 0.1.

TABLE IV. Molecular constants for HCCP, DCCP, and $H^{13}C^{13}CP$ (MHz).

	HCCP	DCCP	$H^{13}C^{13}CP$
B_0	5623.111 558 (58)[a]	5140.236 64 (159)	5396.348 60 (69)
D_0	0.001 537 31 (43)	0.001 211 14 (78)	0.001 413 03 (40)
λ	63 429.42 (111)	63 565.9 (186)	63 467.9 (29)
λ_D	0.024 47 (52)	0.020 92 (57)	0.023 21 (52)
γ	-30.092 (22)	-27.455 (108)	-28.832 (31)
$b_F(P)$	145.71 (147)		140.6 (78)
$c(P)$	-418.9 (59)		-443.9 (167)
$b_F(H)$	-26.34 (180)		
$c(H)$	21.8 (144)		

[a]Values in parentheses denote three times the standard deviation and apply to the last digits of the constants.

$$H = H_{\text{rot}} + H_{\text{ss}} + H_{\text{sr}} + H_{\text{hf},s}(P) + H_{\text{hf},s}(H),$$

where H_{rot} denotes the rotational Hamiltonian with its centrifugal distortion effect, H_{ss} the spin–spin interaction Hamiltonian including its centrifugal distortion effect, H_{sr} the spin–rotation interaction, and $H_{\text{hf},s}(X)$ the hyperfine interaction for the nucleus X. Matrix elements for the above Hamiltonian have been derived by standard methods[31] with the basis function of $|NSJI(P)F_1I(H)FM_F\rangle$, where the coupling scheme used is $J = N + S$, $F_1 = J + I(P)$, and $F = F_1 + I(H)$. A least-squares fitting program[1] was utilized to analyze observed spectral lines and the derived energy matrices were numerically diagonalized to obtain the required energy levels.

For a typical $^3\Sigma$ state, three fine structure components for each rotational level are observed, F_1, F_2, and F_3. Each of these components is then split into two by the hyperfine interaction of the phosphorus nucleus of $I(P) = \frac{1}{2}$ and further split into another two lines by the hyperfine interaction of the hydrogen nucleus of $I(H) = \frac{1}{2}$.

In the initial analysis of the observed spectral lines, the sign of the spin–spin coupling constant, λ, was uncertain, in that both a negative and positive sign of λ gave a good fit of the observed lines, thereby generating two sets of molecular constants to explain the observed line frequencies, both of which caused no sizable change in the overall rms error. No spectroscopic information, neither theoretical nor experimental, as discussed in the Introduction, is available at all to guide such a decision as regarding the sign of λ. If we assume that HCCP has an electronic structure similar to that of HCCN, it is reasonable to take a positive sign for the spin–spin coupling constant of HCCP. This is further confirmed by the assignment of the hyperfine structure due to the hydrogen nucleus and the appropriate sign of the Fermi contact constant for hydrogen. Recorded spectra confirmed that the upper F component for a particular F_1 quantum number of the transitions concerned was of higher frequency than the corresponding lower F component for the same transition when λ was positive and the converse when λ was negative. The correct assignment of the hydrogen hyperfine structure (see Table I) was made on the basis of relative intensities. This assignment was confirmed from the sign of the Fermi contact term of the hydrogen that was found to have the same sign as that of the prototype carbene, CH_2,[32] and also

that of HCCN,[21] and will be described further in the Discussion. Thus, the sign of λ was determined to be positive.

As described before, the hyperfine structure due to the phosphorus nucleus was observed in lower-N transitions from $N = 21 - 20$ and that due to H in lower-N transitions from $N = 11 - 10$, so that all other higher-N hyperfine structure unresolved line frequencies were fitted to calculated frequencies obtained by averaging the frequencies of components weighted in proportion to their relative intensities.[33] Hyperfine splittings due to the deuterium nucleus were not resolved at all for any of the observed lines that were analyzed by using the simple Hamiltonian without hyperfine structure. For $H^{13}C^{13}CP$, the phosphorus hyperfine splitting was only revealed for lower-N transitions from $N = 22 - 21$. Therefore, other higher-N unresolved line frequencies were fitted to calculated frequencies obtained by averaging phosphorus hyperfine structure. The magnitude of the hyperfine splittings due to the hydrogen and ^{13}C nuclei were presumed to be of comparable magnitude (see the Discussion), though this could not be verified. Molecular constants thus determined are given in Table IV.

DISCUSSION

Rotational constants obtained for HCCP, DCCP, and $H^{13}C^{13}CP$ given in Table IV have led to the determination of the r_0 structure of HCCP. The r_0 bond lengths were ascertained as 1.685, 1.241, and 1.057 Å for the CP, CC, and CH bonds, respectively, where their probable errors are estimated to be mainly due to the vibration–rotation effect, and are expected to be significant in the last digits of the bond lengths. The r_0 structure thus obtained is compared with those of related molecules in Table V. A CP bond length of 1.685 Å is compared with the pure triple bond of HCP, 1.5402 Å,[35] the typical double bond of CH_2PH, 1.673 Å,[36] and the single bond of CH_3PH_2, 1.858 Å,[37] and is concluded to be a double bond possessing a small contribution of a single bond feature. The CC bond of 1.241 Å can be compared with that of related molecules; 1.202 41 Å in $HC\equiv CH$,[38] 1.3391 Å in $CH_2=CH_2$,[39] 1.3093 Å in $CH_2=C=CH_2$,[40] 1.323 Å in HCCN,[20] and 1.2539 Å in C_3H.[41] Here it must be noted that the molecular structure of C_3H was explained by a picture made of a roughly equal contribution of the two canonical forms: the acetylene form

TABLE V. Comparison of the structural parameters of HCCP with those of related molecules.

Molecule	r(CP) (Å)	r(CC) (Å)	r(CH) (Å)	Method
HCCP	1.685	1.241	1.057	r_0[a]
CP	1.561 977(7)			r_e, FTIR[b]
HCP	1.540 20(3)		1.0666(2)	r_e, MW[c]
CH$_2$PH	1.673(2)		1.090(15)	r_0, MW[d]
CH$_3$PH$_2$	1.858(3)		1.094(8)	r_g, ED[e]
HC≡CH		1.202 41(9)	1.062 50(10)	r_e, IR,Ra[f]
CH$_2$=CH$_2$		1.3391(13)	1.0868(13)	r_z, MW[g]
CH$_2$=C=CH$_2$		1.3093(7)	1.0865(19)	r_z, ED,MW[h]
HCCN		1.323	0.998	r_s, MW[i]
C$_3$H		1.2539(2)	1.0171(1)	r_s, MW[j]
CH$_2$			1.0766(14)	r_e, combined[k]

[a]The present study.
[b]Reference 34.
[c]Reference 35.
[d]Reference 36.
[e]Reference 37.
[f]The combined analysis of IR and Raman data. Reference 38.
[g]Reference 39.
[h]Reference 40.
[i]Reference 20.
[j]r(CC) for r(C$_\beta$C$_\gamma$). Reference 41.
[k]Combined analysis of known spectroscopic data. Reference 42.

of C–C≡C–H and the allene form of C=C=C–H, though the spin densities on its three carbon atoms are somewhat different from the simple Hückel model. The CC bond length of HCCP is shorter by about 0.01 Å than the C$_\beta$C$_\gamma$ bond length of C$_3$H, indicating that HCCP has a CC bond intermediate between the typical double and triple bonds. The CH bond of 1.057 Å is nearly equal to that of acetylene. These structural features of HCCP suggest that the new phosphorus-bearing carbon chain HCCP almost has the allenic form, which is somewhat modified by a phosphorene feature, resulting in the well-behaved linear radical in the $^3\Sigma$ state. The structural characteristics obtained are also consistent with the spin density of HCCP deduced from the hyperfine coupling constants.

When the unpaired electron around the phosphorus nucleus occupies the p_π atomic orbital, the spin density on the P atom can be estimated by using the corresponding atomic value.[43] Spin density on the P atom is calculated to be 76%. The nonzero Fermi contact term for the P atom can be explained by the spin polarization effect. The negative Fermi contact constant of the hydrogen atom is related to the spin density on the neighboring carbon atom.[44] Spin density for the carbon atom C$_\beta$ adjacent to the hydrogen atom is estimated to be 42% by using the relation for π radicals. The small dipolar coupling constant for the hydrogen atom is consistent with the smaller spin density for the C$_\beta$ atom than that found in HCCN.[20] As discussed above, contribution of the phospho-carbene form is negligible in the structure of HCCP, then the molecular structure of HCCP could be explained by a linear combination of two canonical configurations of phospho-allene and phosphorene forms with an approximate weight of three to one. The structural feature of HCCP presented in this study may be an ideal and challeng-

ing target for high-level quantum mechanical calculations.

The spin density estimated on the C$_\beta$ atom predicts the hyperfine coupling constants c to be about -68 MHz and b_F of a similar magnitude. These hyperfine coupling constants suggest reasonable hyperfine splittings in the lower-N rotational transitions of H^{13}C^{13}CP. However, in the course of this study, it was not possible to resolve such structures for even the lowest rotational transition observed for H^{13}C^{13}CP. Observations of spectral lines resolved for the ^{13}C hyperfine structure of the H^{13}CCP and HC^{13}CP species may be useful to ensure a complete determination of the spin density for each atom of HCCP and a further detailed characterization of its molecular structure.

If the off-diagonal spin–orbit coupling constant of the radical is assumed to be a value averaged over the constituent atoms weighted with their spin densities, 221 cm^{-1},[45] and only one electronically excited state is thought to perturb the ground electronic state, then the observed spin–spin coupling constant λ predicts an excitation energy of about 12 000 cm^{-1} for the $^1\Sigma^+$ state and the observed spin–rotation coupling constant γ gives an excitation energy of about 17 000 cm^{-1} for the $^3\Pi$ state.[46] These results may lead to a further discussion of the electronic structure of HCCP, when experimental and theoretical information will be available on its electronic structure.

In conclusion, the present study has provided the first identification of the phosphorus-bearing carbon-chain radical, HCCP, in the gas phase by microwave spectroscopy. The r_0 structure of HCCP was determined from the rotational constants of the main and isotopically substituted species. The spin density on the phosphorus atom was estimated from the hyperfine structure due to the phosphorus nucleus, and that on the carbon atom adjacent to the hydrogen from the Fermi contact term of the hydrogen. These features conclude that the structure of HCCP is a linear phospho-allenic form that is somewhat modified by a phosphorene. Detailed and precise measured line frequencies of HCCP are now available for its astronomical search in the circumstellar envelopes or dark molecular clouds.

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