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Note

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The microwave spectrum of cyanophosphaacetylene, $H_2P-C\equiv C-C\equiv N$

Lu Kang^a, Andrea J. Minei^b, Stewart E. Novick^{b,*}

^a Department of Natural Sciences, Union College, Barbourville, KY 40906, USA ^b Department of Chemistry, Weslevan University, Middletown, CT 06459, USA

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Abstract

The *a* type transitions of the microwave rotational spectra of cyanophosphaacetylene, $H_2P-C\equiv C-C\equiv N$, have been investigated in the frequency region between 5 and 26.5 GHz by Fourier transformation microwave (FTMW) spectroscopy. Rotational, centrifugal distortion and ¹⁴N nuclear quadrupole coupling constants have been determined. Density functional theory level *ab initio* calculations were performed to predict the molecular constants, and the predicted values are in good agreement with our experimentally determined results. The ¹³C and ¹⁵N isotopomer transitions were also observed. The derived r_0 structure is quite comparable to the calculated $H_2P-C\equiv C-C\equiv N$ equilibrium geometry.

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1. Introduction

We recently published a pulsed-jet Fourier transform microwave (FTMW) study of cyanophosphine, H₂PCN, the first spectroscopic study, at any wavelength, of this simple five-atom phosphine derivative [1]. Almost all the small molecules containing both phosphorous and carbon which have been studied by high resolution microwave spectroscopy involve multiple bonds between the carbon and the phosphorous, usually $C \equiv P$, as presented in reference [1]. The simple phosphine derivatives are as rare as hen's teeth in the microwave literature, perhaps because the syntheses are difficult with immediate rearrangement in basic medium, for example, $N \equiv C - PH_2 \rightarrow H_2N - C \equiv P[2]$. Reactivity is not a concern in in situ discharge sources in FTMW spectrometers, it is only required that the desired molecule be stable with respect to unimolecular dissociation or rearrangement on the time scale of the travel time to the center

* Corresponding author. Fax: +1 860 685 2211.

E-mail address: snovick@wesleyan.edu (S.E. Novick).

of the microwave cavity, ~ 1 ms. In the present study, we present the result of the "next" molecule in this series, when considered as a target for astrophysical detection, cyanophosphaacetylene, H₂P-C=C-C=N.

2. Experimental

The rotational spectra of H₂PCCCN, cyanophosphaacetylene, were recorded with a pulsed-jet Fourier transform microwave spectrometer based on the original design of Balle and Flygare [3]. There is an excellent recent review of the design parameters of FTMW spectrometers by Grabow, et al. [4]. The details of our version of the spectrometer are given elsewhere [5,6]. A mixture of 0.5% cyanoacetylene, 0.5% phosphine, and 99% neon was expanded through a 0.8 mm diameter General Valve nozzle followed by a 900 V pulsed discharge immediately upstream of the nozzle. H₂PCCCN was "synthesized" in sufficient abundance that the signal-to-noise ratio of most of the measured microwave transitions of the normal isotopomer of H₂PCCCN was 5 or 10 to 1 after a few thousand

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Hyperfine components of the 3_{03} - 2_{02} transition of H₂PCCCN



Fig. 1. Three hyperfine components of the $3_{03} - 2_{02}$ transition of H₂PCCCN. This is one of the strongest of the measured transitions. Most of our transitions required thousands of gas pulses to achieve a signal-to-noise ratio of 10/1. This transition was obtained with 256 gas pulses. Multiple microwave pulses were injected into the cavity during each gas pulse. Only 3 or 4 of these microwave pulses per gas pulse contribute significantly to this transition.

shots of the 0.6 ms duration pulsed jet. The cyanoacetylene, $H-C\equiv C-C\equiv N$, was synthesized by the removal of water, using P₂O₅, from commercially available propynoic acid amide, $H-C\equiv C-CONH_2$ [7]. Shown in Fig. 1 is one of the stronger transitions which was obtained after 256 gas pulses with at least three microwave pulses during each gas pulse.

3. Results and analysis

The spectra of five isotopologues of H₂PCCCN were fit using Pickett's spFiT suite of spectra fitting programs.[8,9] Table 1 presents the ninety one $K_a = 0$ and $K_a = 1$ *a*-type transitions and assignments for the normal isotopomer. Tables 2–5 present the $K_a = 0$ *a*-type transitions of the singly-substituted ¹³C or ¹⁵N isotopologues, all measured in natural abundance. The $K_a = 1$ transitions were too weak to measure for the substituted isotopologues.

A density functional B3LYP//6-311++g(d,p)(H,C,N)/ cc-pVQZ(P) *ab initio* optimization calculation was performed on H₂PCCCN [10]. This method and basis set was chosen because it worked well for H₂PCN [1]. Using the *ab initio* spectroscopic constants, it was relatively easy to locate the microwave transitions of the normal and the minor isotopologues of cyanophosphaacetylene. All of the measured spectroscopic constants for all five of the studied isotopologues of H₂PCCCN are given in Table 6. The *A* rotational constants given in Table 6 are from the *ab initio* calculation. The extremely large value of 8.1 MHz for Δ_K presented in Table 6 is also the *ab initio* value. Since all the transitions are *a*-type, $\Delta(K_a) = 0$, the value of Δ_K made no difference to the fit.

B and *C* were both determined for the normal isotopomer. However, for the singly-substituted isotopologues, only

Table 1								
Transition	frequencies	and	assignments	of	the	normal	isotopomer	of
II DCCCN								

$\frac{I_2I}{J'_{v}v}$	$J_{V V}''$	F'	F''	Frequency	Obs – Calc
2_{aa}	1 or	2	2	5287 854	_2
-02	101	1	0	5288.069	1
		2	1	5289 129	_1
		2	2	5289.221	-1
		1	1	5291.254	0
2	2	2	2	7021.000	4
313	212	3	2	7931.099	-4
		4	3	/931.4/5	-3
		2	1	/931.492	2
3 ₀₃	202	3	3	7932.326	-1
		2	1	7933.479	0
		3	2	7933.692	0
		4	3	7933.743	1
		2	2	7935.603	0
312	211	2	1	7936.056	1
4 ₁₄	313	4	3	10575.047	0
		3	2	10575.168	1
		5	4	10575.213	-1
404	303	4	4	10576.833	-1
-04	- 05	3	2	10578 159	0
		4	3	10578 252	1
		5	4	10578 283	0
		3	3	10580.070	0
4	3	4	3	10581 175	0
-13	512	3	2	10581 283	1
		5	4	10581.347	0
-		-		12210.001	3
3 ₁₅	414	5	4	13218.881	2
		4	3	13218.929	0
_		-	-	15210.972	2
5_{05}	4_{04}	5	5	13221.356	-1
		4	3	13222.755	2
		5	4	13222.805	0
		6	5	13222.828	2
		4	4	13224.573	-1
514	413	5	4	13226.542	1
		4	3	13226.581	-1
		6	5	13226.635	0
6 ₁₆	5 ₁₅	6	5	15862.677	1
		5	4	15862.703	3
		7	6	15862.732	0
606	505	6	6	15865.881	$^{-2}$
		5	4	15867.323	3
		6	5	15867.352	-1
		7	6	15867.370	1
		5	5	15869.088	$^{-2}$
615	514	6	5	15871.869	0
15	14	5	4	15871.894	6
		7	6	15871.925	-3
717	616	7	6	18506 454	-1
· 1 /	010	6	5	18506 467	0
		8	7	18506.495	2
7	6.	7	7	18510 407	_1
· 07	006	6	5	18511.40/	_1 _2
		7	6	18511.809	- <u>-</u> 2 1
		8	7	18511 910	3
		6	6	18513.606	-3

Table 2

Table 1 (continued)

$J'_{K_{\mathrm{a}}K_{\mathrm{c}}}$	$J_{K_{\mathrm{a}}K_{\mathrm{c}}}''$	F'	F''	Frequency	Obs – Calc
7 ₁₆	615	7	6	18517.179	-2
		6	5	18517.191	2
		8	7	18517.219	-1
818	717	8	7	21150.217	-4
		7	6	21150.223	-4
		9	8	21150.249	2
808	7 ₀₇	8	8	21154.927	-2
		7	6	21156.410	-1
		8	7	21156.428	1
		9	8	21156.439	2
		7	7	21158.125	-1
817	7 ₁₆	8	7	21162.479	1
		7	6	21162.481	-1
		9	8	21162.508	2
9 ₁₉	818	9	8	23793.974	-1
		8	7	23793.975	-2
		10	9	23793.998	4
9 ₀₉	808	9	9	23799.442	-1
		8	7	23800.938	-1
		9	8	23800.952	1
		10	9	23800.962	3
		8	8	23802.636	-2
9 ₁₈	817	9	8	23807.758	-7
		8	7	23807.764	-1
		10	9	23807.788	3
10110	9 ₁₉	10	9	26437.717	0
		9	8	26437.717	-2
		11	10	26437.735	2
10010	9 ₀₉	10	10	26443.948	-1
		9	8	26445.455	-1
		10	9	26445.467	2
		11	10	26445.475	3
		9	9	26447.140	-1
1019	9 ₁₈	9	8	26453.039	0
		10	9	26453.039	0
		11	10	26453.056	1

(B + C) was determined. Table 6, however, presents B and C separately. This was done by fixing (B - C) in the spectroscopic fit. The various (B - C)'s were calculated from the *ab initio* optimized structure and then this difference was scaled by a constant, 1.01235, given by $(B_{\text{measured}} - C_{\text{measured}})/(B_{\text{calc}} - C_{\text{calc}})$ for the normal isotopomer.

3.1. Structural analysis

Since complete isotopic substitution was not performed on cyanophosphaacetylene (H, and of course, P, not substituted); the A rotational constants were not measured, but calculated; and (B - C)'s were extrapolated from the *ab initio* calculation for the minor isotopologues; the determination of the structure of the molecule involved compromises. The Kraitchman, r_s , positions [11] were determined for the three carbon atoms and the nitrogen atom. These positions were used

Transition frequencies and assignments of the isotopomer H ₂ P ¹³ CCCN						
$J'_{K_{\mathrm{a}}K_{\mathrm{c}}}$	$J_{K_{\mathrm{a}}K_{\mathrm{c}}}''$	F'	F''	Frequency	Obs – Calc	
303	202	2	1	7928.747	0	
		3	2	7928.960	0	
		4	3	7929.010	-1	
404	3 ₀₃	3	2	10571.850	0	
		4	3	10571.944	2	
		5	4	10571.972	-1	
5 ₀₅	404	5	4	13214.918	0	
		6	5	13214.941	0	
606	5 ₀₅	5	4	15857.861	4	
		6	5	15857.885	-4	
		7	6	15857.906	1	
7 ₀₇	606	6	5	18500.822	-9	
		7	6	18500.851	-3	
		8	7	18500.869	3	
808	7 ₀₇	7	6	21143.791	-3	
		8	7	21143.810	1	
		9	8	21143.822	2	
9 ₀₉	808	9	8	23786.758	1	
		10	9	23786.767	3	
10010	9 ₀₉	9	8	26429.680	-3	
		10	9	26429.695	2	
		11	10	26429.704	4	

Table 3			
Transition frequen	ncies and assignm	nents of the isotop	oomer H ₂ PC ¹³ CCN

$J_{K_{\mathrm{a}}K_{\mathrm{c}}}^{\prime}$	$J_{K_{\mathrm{a}}K_{\mathrm{c}}}''$	F'	F''	Frequency	Obs – Calc
303	202	2	1	7922.140	-1
		3	2	7922.353	0
		4	3	7922.405	1
404	303	3	2	10563.040	-1
		4	3	10563.134	2
		5	4	10563.163	-1
606	5 ₀₅	5	4	15844.646	3
		6	5	15844.673	-2
		7	6	15844.693	2
7 ₀₇	6 ₀₆	6	5	18485.410	-4
		7	6	18485.434	-2
		8	7	18485.452	2
808	7 ₀₇	7	6	21126.171	-3
		8	7	21126.191	0
		9	8	21126.203	3
9 ₀₉	808	8	7	23766.922	0
		9	8	23766.937	1
		10	9	23766.945	2
10010	9 ₀₉	9	8	26407.657	-2
		10	9	26407.666	-3
		11	10	26407.679	4

to calculate the r_s distances shown in the second row of bond distances in Fig. 2. An r_0 structure of cyanophosphaacetylene was calculated using Zbigniew Kisiel's STR-FIT program [9]. Ten rotational constants, *B* and *C*

Table 4 Transition frequencies and assignments of the isotopomer $H_2PCC^{13}CN$

$J_{K_{\mathrm{a}}K_{\mathrm{c}}}^{\prime}$	$J_{K_{\mathrm{a}}K_{\mathrm{c}}}''$	F'	F''	Frequency	Obs - Calc
303	202	2	1	7842.744	0
		3	2	7842.956	-1
		4	3	7843.006	-1
4 ₀₄	3 ₀₃	3	2	10457.178	0
		4	3	10457.270	1
		5	4	10457.302	0
6 ₀₆	5 ₀₅	5	4	15685.848	-1
		6	5	15685.876	-5
		7	6	15685.896	-2
7 ₀₇	606	6	5	18300.151	-4
		7	6	18300.175	-3
		8	7	18300.191	2
808	7 ₀₇	7	6	20914.447	-2
		8	7	20914.465	0
		9	8	20914.477	2
9 ₀₉	808	8	7	23528.736	4
		10	9	23528.757	5
10010	9 ₀₉	9	8	26143.003	0
		10	9	26143.012	-1
		11	10	26143.020	0

Table 5 Transition frequencies and assignments of the isotopomer $H_2PCCC^{15}N$

$J'_{K_{\mathrm{a}}K_{\mathrm{c}}}$	$J_{K_{\mathrm{a}}K_{\mathrm{c}}}''$	Frequency	Obs – Calc
303	202	7720.630	0
404	3 ₀₃	10294.170	1
5 ₀₅	4_{04}	12867.700	-4
6 ₀₆	5 ₀₅	15441.233	1
7 ₀₇	606	18014.755	1
808	7 ₀₇	20588.271	0
9 ₀₉	8 ₀₈	23161.779	2
10010	909	25735.275	-1

Table 6	
Spectroscopic constants of H2PCCCNa	,b



Fig. 2. The structure of H₂PCCCN. The least-squares fit, r_0 , structure; the substitutional, r_s , structure; and the *ab initio* structures are given. See text.

from the five studied isotopologues of cyanophosphaacetylene were used to fit four bond lengths and the $P-C \equiv C$ angle. These distances and the angle are given in the first row of Fig. 2. Finally, the calculated B3LYP //6-311++g(d,p)(H,C,N)/cc-pVQZ(P) [10], values of the distances and angles are given in the third row of Fig. 2. These three sets of structural parameters are in good agreement with each other. The C-C bond adjacent to the $C \equiv N$ is presented in the figure as a single bond, but its length is between that of a typical CC single and double bond. The most striking feature of the structure of cyanophosphaacetylene is the nonlinear P-C=C angle of 174°. The analogous angle, P-C=N, in H₂PCN was determined to be 175° [1]. The nitrogen analog of H₂PCN is cyanamide, H₂NCN. A detailed structural determination of cyanamide originally determined that the N-C=N spine was linear [12]. However, a semirigid bender analysis of inverting cyanamide has determined that the N–C \equiv N spine is nonlinear by $\sim 5^{\circ}$ [13]. To the best of our knowledge, the nitrogen analog of cyanophosphaacetylene, aminocyanoacetylene, $H_2N-C\equiv C-C\equiv N$, has not been studied in the microwave. No spectroscopic evidence for measurable (>3 kHz)inversion was detected in either H₂PCN or in H₂PCCCN.

	H ₂ PCCCN	H ₂ P ¹³ CCCN	H ₂ PC ¹³ CCN	H ₂ PCC ¹³ CN	H ₂ PCCC ¹⁵ N
A	128236.5°	128042.2 ^c	128210.7 ^c	128236.4 ^c	128212.6 ^c
В	1323.04891(7)	$1322.24881(5)^{d}$	$1321.15552(4)^{d}$	$1307.90894(4)^{d}$	$1287.4969(1)^{d}$
С	1321.51672(6)	$1320.73961(5)^{d}$	$1319.63052(4)^{d}$	$1306.41144(4)^{d}$	$1286.0481(1)^{d}$
$\Delta_I \times 10^3$	0.0472(3)	h	h	h	0.0428(8)
$\Delta_{IK} \times 10^3$	4.13(3)	h	h	h	h
Δĸ	8.1 ^e	h	h	h	h
γ_{aa}^{R} f	-4.247(1)	h	h	h	
$\chi_{bb} - \chi_{cc}^{f}$	0.64(5)	h	h	h	
N/σ^{g}	91/2 kHz	22/3 kHz	21/2 kHz	20/2 kHz	6/2 kHz

^a All constants in MHz.

^b The numbers in parenthesis are the 1-standard deviation errors.

^c Fixed at the *ab initio* value.

^d (B + C)/2 is fit. (B - C) is fixed to the scaled *ab initio* value; see text.

^e The fit is essentially insensitive to this centrifugal distortion constant. Δ_K is held at the (large) value predicted by the *ab initio* calculation.

^f The nuclear quadrupole coupling constants of ¹⁴N.

^g Number of transitions in the fit/standard deviation of the fit.

^h Fixed to the value of the corresponding constant of the normal isotopomer.

3.2. Nuclear quadrupole coupling constant and bonding

The nitrogen nuclear quadrupole coupling constant is. of course, a measure of the electric field gradient at the nitrogen nucleus of the $-C \equiv N$ group. Nitrile χ_{aa} values range from -2.67(5) MHz in F-C=N [14], through -3.32(2) MHz in H₂N $-C \equiv N$ [15], -4.224(4) MHz in H₃C-C=N [16], to -4.70783(6) MHz in H-C=N [17], from highest to lowest electronegative binding partner to the cyanide. This is an approximately linear relationship between the nitrogen quadrupole coupling constant and the electronegativity of the atom bound to the cyanide. χ_{aa} of H₂PCCCN is -4.247(1) MHz. Since the *a* axis of the molecule is only 1.5° from the CN axis, χ_{aa} is essentially a measure of the field gradient along the CN triple bond. This value is squarely in the middle of the values for CN and is typical of that of $\chi_{aa}(N)$ of ... C—C \equiv N. In contrast, $\chi_{aa}(N)$ in H₂P-C N is -4.589(2) MHz which is similar to that of HCN, as the electronegativity of H and P are similar. The $-C \equiv C -$ "spacer" between the phosphorus and the cyanide in H₂PCCCN mitigates electron donation from the phosphorus into the cyanide. However, the field gradient about nitrogen in H₂PCCCN is not cylindrically symmetrical; $(\chi_{bb} - \chi_{cc}) = 0.64(5)$ MHz, less than that in H₂PCN, 0.765(8) MHz, but not zero. The H₂P-group still serves to distort the field gradient along the nitrogen in cyanophosphaacetylene.

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