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Rotational Spectrum, Structure, and Dipole Moment of Ethynylphosphine, $\text{H}_2\text{PC}\equiv\text{CH}$

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The rotational spectra of ethynylphosphine, $\text{H}_2\text{PC}\equiv\text{CH}$ and $\text{D}_2\text{PC}\equiv\text{CH}$, have been determined in selected regions between 8 and 120 GHz to obtain rotational and centrifugal distortion constants. The substitution coordinates of the P hydrogens have been determined. If a reasonable structure for the ethynyl group is assumed, a $\text{P}-\text{C}\equiv\text{C}$ angle of $173 \pm 2^\circ$ is required to obtain a consistent fit to the moments of inertia. The best determination of the structural parameters is $r(\text{P}-\text{H}) = 1.414$ (5) Å, $r(\text{P}-\text{C}) = 1.774$ (5) Å, $\angle(\text{P}-\text{C}\equiv\text{C}) = 173$ (2) $^\circ$, $\angle\text{H}-\text{P}-\text{H} = 93.9$ (5) $^\circ$, $\angle\text{H}-\text{P}-\text{C} = 96.9$ (5) $^\circ$, $r(\text{C}\equiv\text{C}) = 1.208$ Å (assumed), $r(\text{C}-\text{H}) = 1.058$ Å (assumed), and $\angle(\text{C}\equiv\text{C}-\text{H}) = 180.0^\circ$ (assumed). The dipole moment and the relative signs of its components have been determined. For $\text{H}_2\text{PC}\equiv\text{CH}$, $\mu_a = 0.155$ (1) D, $\mu_c = 0.555$ (1) D, and $\mu_{\text{tot}} = 0.576$ (1) D, and for $\text{D}_2\text{PC}\equiv\text{CH}$, $\mu_a = 0.137$ (2) D, $\mu_c = 0.564$ (3) D, and $\mu_{\text{tot}} = 0.580$ (3) D.

Introduction

Simple bonding theory has been successfully used in many instances to explain the observed structural parameters of compounds containing an sp-hybridized carbon directly bonded to an atom with low-lying d orbitals. The microwave-determined structure of ethynylsilane¹ and ethynylgermane² are consistent with this simple theory. In analogous compounds containing phosphorus, for which a P-C bond colinear with the triple bond is predicted, structural evidence favors a slightly bent configuration. In particular, the crystal structure of phosphorus tricyanide³ and the gas-phase structure of cyanodifluorophosphine^{4,5} have a P-C-N angle of 172° . An electron diffraction study of the structure of this molecule could not determine the P-C-N angle.⁶ Also, crystalline triethynyl phosphine⁷ has a nonlinear P-C≡C structure.

The molecular structures of analogous compounds with a nitrogen atom instead of a phosphorus atom have been determined. The difluorinated amine, difluorocyanamide,⁸ has a bent N-C≡N angle of 174° . However, cyanamide has an additional complexity in its rotational spectrum originating from the inversion of the NH group, which obscures the effect of the small bend in the N-C≡N bond. Early spectroscopic structural determinations of cyanamide assumed a linear bond⁹⁻¹⁴ to reduce the number of unknown parameters in the fitting of the structure. In all these investigations, the studies focused primarily on obtaining the height and the shape of the potential barrier for the inversion of the NH₂ group about the plane. A more recent study indicates that a best fit to the same potential well by all isotopic species of cyanamide can only be obtained if the N-C≡N angle is bent by about 5° .¹⁵ In addition, some ab initio calculations have been carried out to explain the nonlinearity of the bond for these molecules. The first results obtained by using the IBMOL-5 program¹⁶ indicated that NF_2CN and PF_2CN were nonlinear, while NH_2CN was linear. A second study using the STO-3G minimal basis set with the Gaussian 70 program^{17,18} predicted that cyanamide, difluorocyanamide, and dimethylcyanamide all had bent N-C≡N bonds.¹⁹ The molecular structures of analogous molecules containing an acetylene rather than a cyano moiety have not been determined.

This present microwave study was undertaken to determine the configuration of the heavy-atom framework in $\text{H}_2\text{PC}\equiv\text{CH}$. The rotational spectra of both $\text{H}_2\text{PC}\equiv\text{CH}$ and $\text{D}_2\text{PC}\equiv\text{CH}$ have been observed. Rotational constants, centrifugal distortion constants, and the dipole moment have been determined for both species. With assumed C≡C and C-H bond lengths, the remaining structural parameters have been derived by fitting them to the six rotational constants. The heavy-atom framework is shown to be nonlinear. Structural results are compared with those for other

phosphines and ab initio calculations.

Experimental Section

The compound $\text{H}_2\text{PC}\equiv\text{CH}$ was prepared by using a previously described silent electric discharge synthesis.²⁰ $\text{D}_2\text{PC}\equiv\text{CH}$ was synthesized by distilling a large excess of D_2O onto the normal species and allowing the mixture to exchange at room temperature for about 2 h. Spectra were observed on either a conventional 100-kHz Stark modulated spectrometer or a Hewlett-Packard Model 8420 spectrometer modified for high-frequency work. Measurements were made at -78°C or at room temperature and at pressures in the 10-50 mTorr range. The sample cell and vacuum line were exposed to D_2O prior to each run of $\text{D}_2\text{PC}\equiv\text{CH}$ so that the deuterated sample would not exchange with any protonated impurities adsorbed on the walls of the cell. The sample was stable indefinitely at -78°C and, on the basis of its microwave spectrum, showed little deterioration at room temperature over periods of many hours.

Rotational Spectra and Analysis

The rotational spectra of both species are typical of those of near-prolate tops, and showed no evidence of inversion in the ground vibrational state. No excited-state spectra have been observed. The initial assignment of the $\text{H}_2\text{PC}\equiv\text{CH}$ was based on low J a -dipole transitions with subsequent assignment of the c -dipole, $K_a = 1 \leftarrow 0$, Q-branch transitions at higher frequency. For $\text{D}_2\text{PC}\equiv\text{CH}$ only c -dipole transitions were measured as the much weaker a -type lines did not contain any information necessary for the desired analysis. For both species, a sufficient variety of transitions was measured to determine a very accurate set of

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Table I. Observed Transitions of Ethynylphosphine, $H_2PC\equiv CH$

a -type transitions	ν_{obsd}^a MHz	Δ^b kHz	c -type transitions	ν_{obsd}^a MHz	Δ^b kHz
$1_{0,1} \leftarrow 0_{0,0}$	10204.090	-26	$1_{1,0} \leftarrow 2_{0,2}$	104844.304	35
$2_{1,1} \leftarrow 1_{1,0}$	20431.630	-46	$2_{1,1} \leftarrow 3_{0,3}$	94663.763	29
$2_{1,2} \leftarrow 1_{1,1}$	20384.110	-103	$10_{1,9} \leftarrow 11_{0,11}$	13650.001	26
$2_{0,2} \leftarrow 1_{0,1}$	20408.190	-11	$14_{0,14} \leftarrow 13_{1,12}$	16529.371	-34
$3_{2,1} \leftarrow 2_{2,0}$	30610.740	67	$10_{1,10} \leftarrow 10_{0,10}$	124582.348	13
$3_{2,2} \leftarrow 2_{2,1}$	30610.740	67	$11_{1,11} \leftarrow 11_{0,11}$	124451.019	37
$3_{1,2} \leftarrow 2_{1,1}$	30647.410	-20	$12_{1,12} \leftarrow 12_{0,12}$	124307.850	37
$3_{1,3} \leftarrow 2_{1,2}$	30576.180	-57	$13_{1,13} \leftarrow 13_{0,13}$	124152.870	11
$9_{8,1} \leftarrow 8_{8,0}$	91758.400	16	$14_{1,14} \leftarrow 14_{0,14}$	123986.142	-14
$9_{8,2} \leftarrow 8_{8,1}$	91758.400	16	$15_{1,15} \leftarrow 15_{0,15}$	123807.664	-77
$9_{7,2} \leftarrow 8_{7,1}$	91775.975	58	$16_{1,16} \leftarrow 16_{0,16}$	123617.677	21
$9_{7,3} \leftarrow 8_{7,2}$	91775.975	58	$17_{1,17} \leftarrow 17_{0,17}$	123415.947	5
$9_{6,3} \leftarrow 8_{6,2}$	91791.121	7	$18_{1,18} \leftarrow 18_{0,18}$	123202.663	15
$9_{6,4} \leftarrow 8_{6,3}$	91791.121	7	$19_{1,19} \leftarrow 19_{0,19}$	122977.764	-56
$9_{5,4} \leftarrow 8_{5,3}$	91803.938	-37	$20_{1,20} \leftarrow 20_{0,20}$	122741.524	14
$9_{5,5} \leftarrow 8_{5,4}$	91803.938	-37	$21_{1,21} \leftarrow 21_{0,21}$	122493.795	22
$9_{4,5} \leftarrow 8_{4,4}$	91814.494	-10	$23_{1,23} \leftarrow 23_{0,23}$	121964.197	-47
$9_{4,6} \leftarrow 8_{4,5}$	91814.494	-10	$35_{1,35} \leftarrow 35_{0,35}$	117862.124	-53
$9_{3,6} \leftarrow 8_{3,5}$	91822.699	-10	$42_{1,42} \leftarrow 42_{0,42}$	114775.633	30
$9_{3,7} \leftarrow 8_{3,6}$	91822.699	-10	$24_{2,22} \leftarrow 25_{1,24}$	116763.758	33
$9_{2,7} \leftarrow 8_{2,6}$	91828.831	-6	$24_{2,23} \leftarrow 25_{1,25}$	124420.845	-71
$9_{2,8} \leftarrow 8_{2,7}$	91828.436	-4	$25_{2,24} \leftarrow 26_{1,26}$	114526.850	2
$9_{1,8} \leftarrow 8_{1,7}$	91938.676	0	$26_{2,24} \leftarrow 27_{1,26}$	95750.651	10
$9_{1,9} \leftarrow 8_{1,8}$	91725.125	-9	$27_{2,26} \leftarrow 28_{1,28}$	94775.524	17
$9_{0,9} \leftarrow 8_{0,8}$	91832.785	18	$34_{2,32} \leftarrow 35_{1,34}$	11309.011	-23
$12_{4,8} \leftarrow 11_{4,7}$	122415.275	-8	$35_{2,34} \leftarrow 36_{1,36}$	16273.401	-55
$12_{4,9} \leftarrow 11_{4,8}$	122415.275	-8	$37_{1,36} \leftarrow 36_{2,34}$	9892.776	63
$12_{3,9} \leftarrow 11_{3,8}$	122426.229	-17	$38_{1,37} \leftarrow 37_{2,35}$	20506.330	-70
$12_{3,10} \leftarrow 11_{3,9}$	122426.229	-17	$41_{1,41} \leftarrow 40_{2,39}$	32377.110	-40
$12_{2,10} \leftarrow 11_{2,9}$	122434.695	-17	$49_{3,46} \leftarrow 50_{2,48}$	115122.075	32
$12_{2,11} \leftarrow 11_{2,10}$	122433.762	-4	$49_{3,47} \leftarrow 50_{2,49}$	116006.592	33
$12_{1,11} \leftarrow 11_{1,10}$	122580.714	28	$51_{3,48} \leftarrow 52_{2,50}$	94628.320	-28
$12_{1,12} \leftarrow 11_{1,11}$	122296.037	30	$51_{3,49} \leftarrow 52_{2,51}$	95660.324	-29
$12_{0,12} \leftarrow 11_{0,11}$	122439.192	16	$57_{3,54} \leftarrow 58_{2,56}$	33094.980	0

^a Lines have been measured to ± 0.05 mHz. ^b Δ is defined as $\nu_{calcd} - \nu_{obsd}$.

Table II. Observed Transitions of P,P-Dideuterated Ethynylphosphine, $PD_2C\equiv CH^a$

c -type transitions	ν_{obsd}^a MHz	Δ^b kHz	c -type transitions	ν_{obsd}^a MHz	Δ^b kHz
$2_{1,1} \leftarrow 1_{0,1}$	82538.788	-6	$15_{2,13} \leftarrow 16_{1,15}$	29911.650	-21
$3_{1,2} \leftarrow 2_{0,2}$	92337.678	24	$15_{2,14} \leftarrow 16_{1,16}$	37382.025	-8
$2_{1,1} \leftarrow 3_{0,3}$	33959.574	-21	$17_{2,15} \leftarrow 18_{1,17}$	9566.753	45
$4_{1,3} \leftarrow 3_{0,3}^c$	102164.354	192	$18_{2,17} \leftarrow 19_{1,19}$	9741.132	-24
$3_{1,2} \leftarrow 4_{0,4}$	24327.219	-9	$20_{1,19} \leftarrow 19_{2,17}$	10863.460	-9
$9_{0,9} \leftarrow 8_{1,7}$	23409.185	6	$21_{1,21} \leftarrow 20_{2,19}$	8543.285	-39
$10_{0,10} \leftarrow 9_{1,8}$	32869.795	14	$22_{1,21} \leftarrow 21_{2,19}$	31372.625	18
$1_{1,1} \leftarrow 1_{0,1}^c$	62995.878	-196	$28_{3,25} \leftarrow 29_{2,27}$	32388.755	1
$2_{1,2} \leftarrow 2_{0,2}$	62940.279	-7	$28_{3,26} \leftarrow 29_{2,28}$	33522.503	5
$6_{1,6} \leftarrow 6_{0,6}$	62439.908	38	$36_{2,35} \leftarrow 35_{3,33}$	34096.440	17
$10_{1,10} \leftarrow 10_{0,10}$	61502.856	-29	$36_{2,34} \leftarrow 35_{3,32}$	36724.839	-11
$12_{1,12} \leftarrow 12_{0,12}$	60875.168	6	$41_{4,37} \leftarrow 42_{3,39}$	32306.588	-8
$13_{1,13} \leftarrow 13_{0,13}$	60522.522	-25	$41_{4,38} \leftarrow 42_{3,40}$	32425.928	3
$14_{1,14} \leftarrow 14_{0,14}$	60144.570	-4	$49_{3,47} \leftarrow 48_{4,45}$	35807.019	-27
$47_{1,47} \leftarrow 47_{0,47}$	37366.297	7	$49_{3,46} \leftarrow 48_{4,44}$	36103.211	26
$54_{1,54} \leftarrow 54_{0,54}$	31496.011	1	$54_{5,49} \leftarrow 55_{4,51}$	31545.868	-14
$55_{1,55} \leftarrow 55_{0,55}$	30675.658	-2	$54_{5,50} \leftarrow 55_{4,52}$	31556.642	15
$56_{1,56} \leftarrow 56_{0,56}$	29862.208	-3			

^a Lines have been measured to ± 0.05 mHz. ^b Δ is defined as $\nu_{calcd} - \nu_{obsd}$. ^c These lines were not used in the fitting.

rotational constants and a complete set of quartic centrifugal distortion constants. These transitions are listed in Tables I and II, which also show the deviations of the spectrum from calculations based on the parameters in Table III. These parameters are defined in the Hamiltonian given by

$$H = AP_a^2 + BP_b^2 + CP_c^2 - D_J P^4 - D_{JK} P^2 P_a^2 - D_K P_a^4 + d_1 P^2 (P_+^2 + P_-^2) + d_2 (P_+^4 + P_-^4) + H_J P^6 + H_{JK} P^4 P_a^2$$

where

$$P_{\pm} = P_b \pm iP_c$$

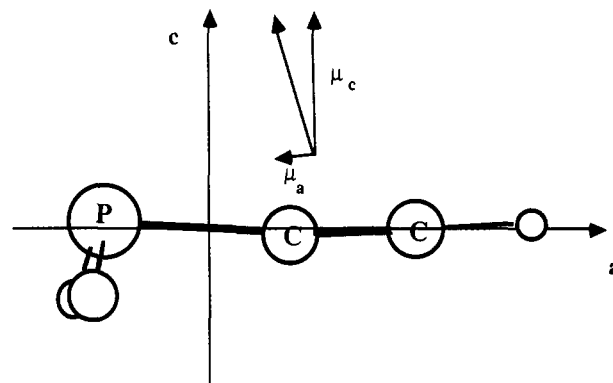
The sextic constants are not meaningful as they are highly correlated and, in addition, do not reflect the uncertainties of other

Table III. Rotational Constants and Moments of Inertia of the Isotopic Species of Ethynylphosphine

	$H_2PC\equiv CH$	$D_2PC\equiv CH$
A , MHz	130345.248 (16)	67882.493 (18)
B , MHz	5113.92758 (76)	4885.7489 (15)
C , MHz	5090.19602 (72)	4830.1606 (15)
D_K , MHz	2.4525 (27)	0.5517 (31)
D_{JK} , MHz	0.064943 (34)	0.05927 (11)
D_J , MHz	0.00135131 (80)	0.0011717 (28)
d_1 , kHz	-0.007157 (30)	-0.015350 (94)
d_2 , kHz	-0.0013191 (36)	-0.004282 (19)
H_{JK} , Hz	0.081 (22)	0.219 (41)
H_J , Hz	-0.00165 (29)	0.00019 (94)
rms, MHz	0.036	0.020
I_a , amu \AA^2	3.877211	7.444865
I_b , amu \AA^2	98.823457	103.438799
I_c , amu \AA^2	99.284192	104.629233
P_{aa} , amu \AA^2	97.115219	100.311584
P_{bb} , amu \AA^2	2.168973	4.317650
P_{cc} , amu \AA^2	1.708238	3.127215

Table IV. Atomic Coordinates in Ethynylphosphine, $H_2PC\equiv CH$

atom	coordinates, \AA		
	a	b	c
H ₁	-1.272	1.033	-0.868
H ₂	-1.272	-1.033	-0.868
P	-1.044	0	0.070
C ₁	0.725	0	-0.052
C ₂	1.932	0	0.012
H ₃	2.988	0	0.068

**Figure 1.** Structure, orientation of principal axes, and dipole moment components in $H_2PC\equiv CH$.

sextic constants excluded from the fit. They are, however, necessary for the fit to accommodate some high- J transitions whose asymmetry splittings contain information on the quartic constants. H_J for the deuterated species is much smaller than its uncertainty but has been kept for consistency with the normal species. The data allow a sensibly small limit to be put on its magnitude.

The uncertainties of the reported parameters are 1σ uncertainties based on an estimated error of ± 50 kHz for each line included in the fit. One extra digit has been kept in both the data and the parameters so that the reader can reproduce the numerical results.

Molecular Structure

The most significant issue in the structure determination of this compound concerns the linearity of the heavy-atom framework. The carbon atoms and the ethynyl hydrogen are expected to lie very close to the molecular a axis as shown in Figure 1. As a result their c coordinates determined by the Kraitchman method are subject to large uncertainties due to zero-point vibrational effects.²¹ The ^{13}C species were not readily assigned in natural

(21) Kraitchman, *J. Am. J. Phys.* 1951, 21, 17.

Table V. Bond Distances and Angles in Ethynylphosphine, $\text{H}_2\text{PC}\equiv\text{CH}$

	exptl	ab initio calcn
$r(\text{P-H})$, Å	1.414 (5)	1.420 (fixed)
$r(\text{P-C})$, Å	1.774 (5)	1.769
$r(\text{C}\equiv\text{C})$, Å	1.208 (assumed)	1.192
$r(\text{C-H})$, Å	1.058 (assumed)	1.060 (fixed)
$\angle(\text{H-P-H})$, deg	93.9 (5)	94.8
$\angle(\text{H-P-C})$, deg	96.9 (5)	97.6
$\angle(\text{P-C}\equiv\text{C})$, deg	173 (2)	176.9
$\angle(\text{C}\equiv\text{C-H})$, deg	180.0 (assumed)	179.9

abundance. However, it was decided to forgo enrichment in those atoms and to isotopically substitute the easily exchanged phosphine hydrogens.

The substitution coordinates are given in Table IV along with the H-H and D-D bond distances determined from the molecular aplanarity. The hydrogen c coordinate is at least 0.02 Å shorter than is necessary to give the observed A rotational constant in a linear-framework molecule. For the deuterated species the difference is about 0.01 Å. This corresponds to a 0.01-Å shrinking on deuteration of the P-H bond projection on an axis in the plane of symmetry perpendicular to the linear frame. In light of the much smaller isotope effects observed in PH_3 and PD_3 ,²² this seems to be an unreasonably large difference. If additional off axis mass is attributed, at least in part, to a bent frame, this difference is reduced and becomes zero for the structure determined below.

The P-C≡C angle and the P-C bond length are readily obtained in the following way. Having determined the H substitution coordinates, the contribution of the hydrogens to the moments can be subtracted from the moments of inertia, and a new axis system, new moments of inertia, and new planar moments (which we call the residual planar moments) are determined for the $\text{PC}\equiv\text{CH}$ frame.²³ These are given in Table IV. Ideally, if the molecular frame (without the hydrogen atoms) were linear, these residual planar moments, P_{bb} and P_{cc} , would be identically zero. Normally, deviations from zero, often called inertial defects, occur due to vibrational zero-point effects. The magnitudes of P_{bb} and P_{cc} should be the same. However, this is not the case. The residual planar moment in the direction perpendicular to the original plane of symmetry, P_{bb} is 0.0166 amu Å, a reasonable value for an inertial defect. It can, of course, be reduced to zero by using the effective H coordinates determined from the nonplanarity instead of the values determined by the Kraitchman substitution method. The residual planar moment in the plane of symmetry is 0.0778 amu Å.

Assuming that the C≡C-H structure is identical with that in ethynylsilane,¹ all the remaining parameters can be determined by fitting the structure to the residual planar moments. The P-C bond length and P-C≡C angle are adjusted to reproduce the calculated planar moments of the PCCH frame. The calculated value for the P-C≡C angle is not sensitive to reasonable assumptions about the C≡C-H structure. The hydrogens are then replaced at the appropriate positions to complete the structure. The resulting parameters are given in Table IV.

The substitution coordinates are consistent with a P-C≡C angle of 173.0° as shown in Figure 1, and the C≡CH group must be bent away from the phosphine hydrogens to be consistent.

As previously mentioned, the rotational constants for each species can be reproduced with the assumption of a linear frame only if a large variation in the effective hydrogen coordinates is allowed on deuteration. Since this variation is in the direction expected for a shortening of the effective P-H bond, the use of effective hydrogen coordinates may lead to the calculation of a larger P-C≡C angle, i.e. less bending. However, lowering the bend by more than 2° introduces the need for changes on deuteration which are considerably larger than those observed in phosphine. For example, if one fixes the H-P-H and H-P-C

angles at the values in Table V and fits the normal species rotational constants by varying only the P-H and P-C bond lengths and the P-C-C angle, one obtains effective P-H and P-C distances of 1.4196 and 1.772 Å and a P-C-C angle of 174.57°. This angle is about 1.5° closer to linearity than that determined directly from the substitution coordinates. Although a number of assumptions have been made, the difference is indicative of expected vibrational contributions to the determination of the angle. At this angle the rotational constants for the deuterated species require that the effective P-D length and D-P-D and D-P-C angles be 1.4161 Å, 96.81°, and 93.96°, respectively. These are comparable to changes observed between PH_3 and PD_3 , but are already somewhat larger.

Dipole Moment

The a and c components of the dipole moment have been determined for both the H_2P and D_2P isotopic species. This was done in order to ascertain the direction of the small μ_a component relative to that of μ_c . For the normal species, several M components of the $10_{1,9} \leftarrow 11_{0,11}$ transition were measured at fields up to 4400 V/cm to determine accurate values of the second-order Stark coefficients A and B in the relationship

$$\Delta\nu = A + BM^2$$

The A coefficient of this transition depends almost entirely on μ_c , and it is very precisely determined. The value of μ_c and the preliminary value of μ_a determined from A and B were used to calculate the second-order contribution to the Stark shift of the $M = 1$ component of the $1_{1,0} \leftarrow 2_{0,2}$ transition. This shift depends primarily on the interaction of the $1_{1,0}$ and $1_{1,1}$ levels via the a dipole for which the two-level problem must be solved by direct diagonalization. After correction for second-order effects, μ_a is given by

$$\mu_a = [\Delta\nu(\Delta\nu + \nu)]^{1/2}/0.25172E$$

where $\Delta\nu$ is the absolute value of the corrected Stark shift in MHz, ν is the frequency of the $1_{1,0} \leftarrow 1_{1,1}$ transition, and E is the field in V/cm. This provided a much more precise value for μ_a . Table VI summarizes the Stark effect data.

For the PD_2 species, the Stark effects of the $2_{1,1} \leftarrow 3_{0,3}$, $1_{1,1} \leftarrow 1_{1,0}$, and $2_{1,2} \leftarrow 2_{0,2}$ transitions were observed. Only the $M = 0$ component of the first transition was measured because it shows well-behaved quadratic behavior and is dependent almost entirely on μ_c . The Stark effect of the $1_{1,1} \leftarrow 1_{0,1}$ transition was fitted in the same manner as that of the normal species with μ_c fixed. For the last transition, second-order Stark coefficients could be obtained by a least squares fit of $\Delta\nu/E^2$ vs E^2 . The results are consistent with those obtained from the first two transitions but are less precise because of a high degree of correlation between μ_a and μ_c and because an exact solution of the Stark effect problem is required. Only the results of the first two transitions are used in the final determination of the $\text{D}_2\text{PC}\equiv\text{CH}$ dipole moment. The results are given in Table VII.

The measurements show that the dipole moments for the normal and deuterated species are 0.575 and 0.580 D respectively in the direction shown in Figure 1. The difference may not be significant since transitions of quite different J are used in determining the larger μ_c component. The angle of rotation of the axes on substitution is 1.26° from the structural determination whereas the apparent rotation angle determined from the dipole moment is 1.8°. Since the assumption that the H-P-C angle is constant with isotopic substitution is not entirely valid and since dipole moments are known to change slightly on deuteration, the source of this difference is ambiguous. The value of the dipole moment is remarkably close to that of phosphine (0.547 D)²⁴ and makes angles of 53.4 and 70.5° with the P-H and P-C bonds respectively. This shows that the projection of the dipole along the P-C direction has the same sign but somewhat smaller magnitude than that along the P-H direction.

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Table VI. Stark Effect in Ethynephosphine, H₂PC≡CH

Second-Order Stark Effects					
transition	M values	Stark coeff, ((Δν cm)/E ²) × 10 ⁶		dipole moment, D	
		obsd	calcd	μ _a	μ _c
H ₂ PC≡CH					
10 _{1,9} ← 11 _{0,11} ^a	10	0.4663 ^a	0.4685		
	9	0.6358	0.6381		
	8	0.7913	0.7899		
	7	0.9256	0.9237	0.160 (20) ^b	0.5549 (6)
	6	1.0410	1.0398		
	5	1.1377	1.1380		
	4	1.2165 ^a	1.2183		
	3	1.2771	1.2808		
1 _{1,0} ← 2 _{0,2}	0	0.2514 (30)		0.1552 ^c	0.5565 (30)
D ₂ PC≡CH					
2 _{1,1} ← 3 _{0,3}	0	0.6737		0.138 (50)	0.5637 (30)
2 _{1,2} ← 2 _{0,2} ^d	1	-0.4410 (40)		0.1374 (20)	0.552 (20)
	2	-2.361 (40)			
First-Order Stark Effect					
	M value	E, V/cm	ΔE, MHz	μ _a , D	μ _c , D
H ₂ PC≡CH					
1 _{1,0} ← 2 _{0,2}	1	447	9.23	0.1546	0.555
	1	886	24.82	0.1550	0.555
	1	1324	41.53	0.1554	0.555
D ₂ PC≡CH					
1 _{1,1} ← 1 _{0,1}	1	447	-4.009	0.1393	0.564 ^c
	1	886	-13.252	0.1384	0.564 ^c
	1	1324	-25.252	0.1389	0.564 ^c
	1	1759	-37.771	0.1382	0.564 ^c
	1	2192	-50.710	0.1378	0.564 ^c

^aNot used in the calculations. ^bThis component was not well determined from this transition. ^cHeld fixed during this calculation because this transition was insensitive to this dipole moment component. ^dNot used in the final determination of the dipole moments.

Table VII. Final Values for the Dipole Moment of Ethynephosphine, H₂PC≡CH

	exptl		HF 3-21g* H ₂ PC≡CH
	H ₂ PC≡CH	D ₂ PC≡CH	
μ _a , D	0.155 (1)	0.138 (1)	0.473
μ _c , D	0.555 (1)	0.564 (3)	0.705
μ _{total} , D	0.576 (1)	0.580 (3)	0.849

Discussion

In Table VIII, we tabulate for comparison the nonlinear angle of some analogous compounds. It is apparent that the nonlinearity of the acetylene angle is not related to d orbitals because, then,

Table VIII. Comparison of the Molecular Structures of H₂PC≡CH and Similar Molecules (X = N, P; Y = C, N)

	∠X—C≡Y, deg	r(X—C), Å	ref
F ₂ P—C≡N	171.2	1.815	4
F ₂ N—C≡N	173.9	1.386	8
H ₂ N—C≡N	175	1.330	15
H ₂ P—C≡CH	173.0	1.774	this work

cyanamide and difluorocyanamide would have linear N—C—N bonds. Also, the bent bond is not a peculiarity of only the CN group but depends on the interaction of the lone pair with the triple bond of the C—N or C—C moiety. The PH₂ structure is similar to that of PH₃, and the H—P—C angle is also close to that in similar molecules. The P—C distance is extremely short, however.

Ab initio calculations were carried out by using Gaussian 82 in the HF3-21g* mode including d orbitals on the phosphorus and optimization of the critical molecular structure parameters. All the bond lengths and angles except the P—H and C—H bond lengths were allowed to vary freely. The final optimized structure predicts a bent P—C≡X angle of 176.9°. The optimized theoretical structure is included in Table V for comparison. The ∠C≡C—H angle is found to be 179.9°, indicating that it remains linear. We also carried out ab initio calculations with Gaussian 82 using a STO 3g minimal basis set to try to identify the interaction responsible for the bending of the P—C—C bond. Calculations with a linear structure and with a bent structure were carried out and compared. No unique, simple model is forthcoming. MO's involving the π orbitals on the acetylene group and the lone pair on the phosphorus are changed by the bending. However, the total effect is an accumulation of a number of small changes in the energy of these orbitals as well as smaller effects in other orbitals.

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