

Spectroscopic and Quantum Chemical Study of Cyclopropylmethylphosphine, a Candidate for Intramolecular Hydrogen Bonding

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The properties of the novel compound cyclopropylmethylphosphine ($C_3H_5CH_2PH_2$) have been investigated by means of Stark-modulation microwave spectroscopy and high-level quantum chemical calculations. Spectra attributable to the three conformers of the molecule with a synclinal arrangement of the H–C–C–P atoms were recorded and assigned. The experimental rotational constants obtained for these conformers were found to be in good agreement with those generated by ab initio geometry optimizations at the MP2/aug-cc-pVTZ level of theory. An estimate of the relative energies of the three conformers with observable spectra, by means of relative intensity measurements, compared favorably with the results of G3 energy calculations performed for the molecule. In addition to the observation of ground-state rotational spectra for three conformers, spectra belonging to a number of vibrationally excited states were also assigned with the aid of radio frequency microwave double-resonance experiments. A tentative assignment of these excited-state spectra was proposed by appealing to the results of density functional theory vibrational frequency calculations performed at the B3LYP/6-311++(3df,2pd) level. The energetically preferred conformer of the molecule allowed a close approach between a hydrogen atom belonging to the phosphino group and the edge of the cyclopropyl ring. The possibility of the formation of an intramolecular hydrogen bond to electron density associated with so-called banana bonds is discussed.

Introduction

The properties of a small number of phosphines have been investigated by means of gas-phase microwave spectroscopy, revealing a unique set of conformational, dynamical, and structural properties. The molecules studied so far include ethylphosphine ($CH_3CH_2PH_2$),¹ 3-phosphinopropionitrile ($H_2PCH_2CH_2C\equiv N$),² 1,2-diphosphinoethane ($H_2PCH_2CH_2PH_2$),³ 2-propynylphosphine ($HC\equiv CCH_2PH_2$),⁴ and 2-propenylphosphine ($H_2C=CHCH_2PH_2$).⁵ The study of small phosphine molecules is hindered by the tendency of these compounds to be toxic, pyrophoric, and particularly malodorous. In addition to these properties, the lack of stability displayed by phosphines in the presence of small quantities of air requires that special care must be taken to avoid polymerization occurring during the experimental process.

The subject of the present investigation, namely cyclopropylmethylphosphine, has been chosen in order to expand the currently limited knowledge of the properties of molecules containing the $-PH_2$ group, with particular reference to the ability of such species to form intramolecular hydrogen bonds. It has been previously noted that the analogous amine species, cyclopropylmethylamine,⁶ has two low-energy conformers that appear to be stabilized by intramolecular hydrogen bonding between the amine group and electron density along the side of the cyclopropane ring. It is therefore of interest to determine whether the energetically preferred conformers of cyclopropyl-

methylphosphine adopt configurations in which the formation of intramolecular hydrogen bonds is possible. It was also hoped that, by comparing the structures of the preferred conformers of cyclopropylmethylphosphine with those of cyclopropylmethylamine, the tendency of P–H groups to form hydrogen bonds could be studied.

Figure 1 shows the five conformers in which cyclopropylmethylphosphine may exist. It can be seen that conformers I, II, III, and IV have the potential for a close approach between a P–H group and the center of a C–C bond on the cyclopropyl group, which may result in these conformers being stabilized by intramolecular hydrogen bonds. In the case of conformer V, however, there is no possibility of such an intramolecular interaction occurring.

Experimental Section

Microwave Experiment. The microwave spectrum of cyclopropylmethylphosphine was measured in the 12–62 GHz frequency range on the Stark spectrometer at the University of Oslo, which has been described elsewhere.⁷ Both Stark-modulation microwave spectroscopy and radio frequency microwave double-resonance (RFMWDR) experiments, similar to those described by Wodarczyk and Wilson,⁸ were employed during the course of the investigation.

The sample of cyclopropylmethylphosphine used during the course of the investigation was stored at a temperature of approximately $-30\text{ }^\circ\text{C}$ prior to use. A solid deposit, presumably an oxidation product, was seen to form over a number of months, although this impurity was believed to have a negligible vapor pressure and therefore had no discernible influence on

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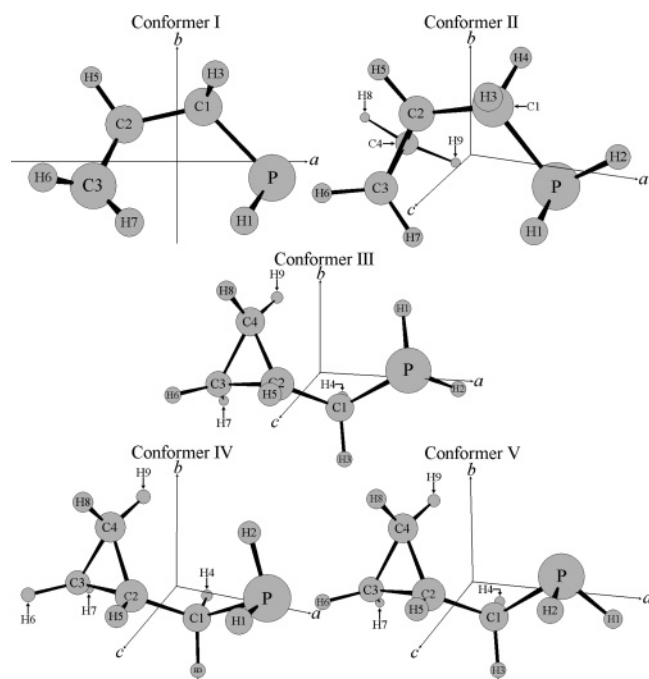


Figure 1. Structures of the five possible conformers of cyclopropylmethylphosphine, as obtained from ab initio geometry optimizations carried out at the MP2/aug-cc-pVTZ level of theory with the Gaussian 03 electronic structure package.⁹ The conformers are shown drawn to scale in the principal inertial axis system.

the observed spectrum. The Stark cell used during the recording of spectra was cooled with a quantity of solid CO₂ to a temperature of around -50 °C, with the aim of increasing the intensity of the spectrum.

Preparation of Cyclopropylmethylphosphine. The following procedure was employed in this first synthesis of cyclopropylmethylphosphine:

Cyclopropylmethylphosphonic Acid, Diethyl Ester. In a one-necked round-bottomed flask were introduced the triethyl phosphite (16.6 g, 0.1 mol), bromomethylcyclopropane (13.5 g, 0.1 mol), and toluene (10 mL). The mixture was heated under reflux overnight and then distilled in vacuo. The cyclopropylmethylphosphonic acid diethyl ester (15.0 g, 78 mmol) was obtained in 78% yield, bp_{0.1} 68 °C. ¹H NMR (400, MHz, CDCl₃) δ 0.17 (m, 2H, CH₂), 0.53 (m, 2H, CH₂), 0.90 (m, 1H, ³J_{HH} = 7.6 Hz, CH), 1.29 (dt, 6H, CH₃), 1.65 (dd, 2H, ³J_{HH} = 7.1 Hz, ²J_{PH} = 17.6 Hz, CH₂P), 4.07 (m, 4H, ³J_{HH} = 7.1 Hz, CH₂O). ¹³C NMR (CDCl₃, 100 MHz) δ 4.19 (dt, ³J_{PC} = 5.6 Hz), 5.10 (dt, ³J_{PC} = 10.5 Hz, ¹J_{CH} = 165.4 Hz), 16.4 (dq, ³J_{PC} = 5.6 Hz, ¹J_{CH} = 126.9 Hz), 30.7 (dt, ¹J_{PC} = 140.6 Hz, ¹J_{CH} = 136.5 Hz), 61.3 (dt, ²J_{PC} = 7.2 Hz, ¹J_{CH} = 146.0 Hz). ³¹P NMR (CDCl₃, 162 MHz) δ 32.0. HRMS. Calcd for C₈H₁₇O₃P: 192.0915. Found: 192.091. IR (neat) ν (cm⁻¹): 2981.8 (s), 2933.7 (m), 2906.4 (m), 1391.6 (m), 1257.3 (s), 1029.7 (s), 959.0 (s), 796.7 (m).

Cyclopropylmethylphosphine. Caution: Cyclopropylmethylphosphine is pyrophoric and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.

The apparatus was similar to that employed for the preparation of 2-propynylphosphine.⁴ In a 250 mL two-necked flask were introduced the reducing agent (LiAlH₄, 0.76 g, 20 mmol) and tetraglyme (50 mL). The flask was attached to a vacuum line, immersed in a cold bath (0 °C), and degassed. The cyclopropylmethylphosphonic acid diethyl ester (1.92 g, 10 mmol) in tetraglyme (10 mL) was slowly added with a flex-needle through the septum for about 5 min. During and after the addition, the

formed cyclopropylmethylphosphine was distilled off in vacuo from the reaction mixture. A cold trap (-80 °C) selectively removed less volatile products and the cyclopropylmethylphosphine was condensed in a second cold trap (-120 °C) to remove the most volatile products (mainly PH₃). After disconnection from the vacuum line by stopcocks, the product was kept at low temperature (<-30 °C) before analysis. The cyclopropylmethylphosphine was obtained in 84% yield (0.74 g). ¹H NMR (400 MHz, CDCl₃) δ 0.13 (m, 2H, CH₂), 0.54 (m, 2H, CH₂), 0.85 (m, 1H, ³J_{HH} = 7.1 Hz, CH₂), 1.46 (tdd, 2H, ³J_{HH} = 7.4, 7.1 Hz, ²J_{PH} = 4.3 Hz, CH₂P), 2.76 (dt, 2H, ¹J_{PH} = 194.8 Hz, ³J_{HH} = 7.4 Hz, PH₂). ¹³C NMR (CDCl₃, 100 MHz) δ 6.3 (dt, ³J_{PC} = 4.0 Hz, ¹J_{CH} = 157.4 Hz), 13.8 (dd, ²J_{PC} = 3.7 Hz, ¹J_{CH} = 154.2 Hz), 19.5 (dt, ¹J_{PC} = 7.3 Hz, ¹J_{CH} = 126.9 Hz). ³¹P NMR (CDCl₃, 162 MHz) δ -138.6. HRMS. Calcd for C₄H₉P: 88.04419. Found: 88.0443. IR (neat) ν (cm⁻¹): 2958.8 (s), 2896.2 (m), 2297.6 (vs) ν_{PH}, 1461.6 (w), 1085.4 (m), 845.6 (m), 643.3 (w).

Results

Quantum Chemical Calculations. The properties of cyclopropylmethylphosphine were investigated by quantum-chemical calculations, by use of a variety of methods and levels of theory. All calculations were performed using the University of Oslo's 64-processor HP "Superdome" facilities and the Gaussian 03 electronic structure package.⁹ Geometry optimizations for the five possible conformations of the molecule were performed by means of self-consistent field calculations, in which the effects of electron correlation were included by use of second-order Møller–Plesset perturbation theory.¹⁰ The basis sets employed in these calculations were 6-311++(3df,2pd)^{11,12} and Dunning's extensive, correlation-consistent aug-cc-pVTZ,¹³ which possesses polarized functions for valence electrons and is augmented with additional diffuse functions. It has been previously noted¹⁴ that the use of a large basis set in an MP2 calculation can provide accurate rotational constants for a molecular system, that is A_e, B_e, and C_e can be calculated to within 1% of the values of A₀, B₀, and C₀ derived from experiment. In addition to these calculations, the geometries of the five conformers were also optimized in a series of density functional theory calculations, by use of the B3LYP three-parameter hybrid functional (Becke's three-parameter functional,¹⁵ employing the Lee, Yang, and Parr correlational functional¹⁶) in conjunction with the 6-311G++(3df,2pd) basis set. Predictions of the quartic centrifugal distortion constants in Watson's A-reduction¹⁷ were also made at this level of theory. Because of the computationally demanding nature of such calculations, the prediction of centrifugal distortion constants was undertaken by a density functional theory (DFT) method, to reduce the amount of processor time used. In the past experience of the authors, the B3LYP/6-311G++(3df,2pd) level of theory generally provides accurate predictions of the quartic centrifugal distortion constants, as well as the components of the electric dipole moment, for small molecules such as that investigated here. The spectroscopic constants obtained from these calculations are presented in Table 1. In addition to these geometry optimizations, G3 energy calculations¹⁸ were performed with the optimized geometries obtained at the MP2/aug-cc-pVTZ level as a starting point. Table 2 provides a comparison of the calculated relative energies of the five conformers of cyclopropylmethylphosphine.

The structures obtained for the five conformers from the geometry optimizations at the MP2/aug-cc-pVTZ level of theory are given, drawn to scale in their principal inertial axis systems, in Figure 1.

TABLE 1: Comparison of the Spectroscopic Constants Obtained for Three Conformers of Cyclopropylmethylphosphine, from Quantum Chemical Calculations and Experiment

spectroscopic constant	conformer III			conformer IV			conformer V		
	B3LYP/6-311++(3df,2pd)	MP2/aug-cc-pVTZ	experiment	B3LYP/6-311++(3df,2pd)	MP2/aug-cc-pVTZ	experiment	B3LYP/6-311++(3df,2pd)	MP2/aug-cc-pVTZ	experiment
<i>A</i> /MHz	11 080.5231	10 902.8365	10 878.235(17)	11 148.2804	11 000.5570	10 959.4(32)	10 976.7989	10 827.8621	10 784.640(9)
<i>B</i> /MHz	1938.8496	2007.5552	1984.7682(19)	1905.0401	1963.8649	1945.130(9)	1954.4473	2019.9099	2000.0835(16)
<i>C</i> /MHz	1795.9154	1851.2838	1831.6144(18)	1773.0054	1821.5779	1804.566(9)	1810.9803	1864.6802	1846.6393(16)
Δ_J /kHz	0.64		0.650(5)	0.52		0.536(8)	0.69		0.772(3)
Δ_{JK} /kHz	-4.41		-4.42(4)	-3.34		-3.29(9)	-5.36		-5.272(9)
Δ_K /kHz	29.24		25.98(24)	26.12			32.70		30.6(5)
δ_J /kHz	0.10		0.1003(3)	0.07			0.10		0.11613(8)
δ_K /kHz	2.30		2.09(13)	1.90			2.04		2.52(2)

TABLE 2: Comparison of the Relative Energies of Five Conformers of Cyclopropylmethylphosphine, from Quantum Chemical Calculations and Experiment^a

method	conformer				
	I	II	III	IV	V
B3LYP/6-311++G(3df,2pd)	+10.2	+9.1	+1.7	0.0	+2.3
MP2/6-311++G(3df,2pd)	+8.6	+8.5	+2.0	0.0	+2.6
MP2/aug-cc-pVTZ	+7.7	+7.5	+1.9	0.0	+2.6
G3	+8.3	+7.9	+2.0	0.0	+2.6
experimental			+1.7	0.0	+2.4

^a All energies are given in kilojoules per mole.

Assignment of Conformer IV. The first attempts to assign the microwave spectrum of cyclopropylmethylphosphine focused on the conformer labeled IV in Figure 1. This conformer was predicted to be the lowest in energy by all of the calculations performed during the course of this study, as can be seen from Table 2. An initial prediction of the rotational spectrum of this conformer was obtained in order to aid the assignment of the microwave spectrum, by using rotational constants from the geometry optimization at the MP2/aug-cc-pVTZ level and centrifugal distortion constants from the B3LYP/6-311G++(3df,2pd) calculation. The spectrum assigned with the aid of this model was that of a nearly prolate asymmetric rotor, in which only a-type transitions, allowed by the component μ_a of the molecular electric dipole moment μ along the principal inertial axis *a*, were sufficiently intense to allow measurement. This observation is consistent with the estimates of the molecular electric dipole moment components obtained from the geometry optimization at the B3LYP/6-311++(3df,2pd) level, which, for conformer IV, predicted $\mu_a = -1.26$ D, $\mu_b = -0.12$ D, and $\mu_c = 0.26$ D.

The experimentally determined rotational transition frequencies were subjected to a least-squares analysis, by use of Sørensen's Rotfit program.¹⁹ The Hamiltonian employed was that appropriate for a semirigid asymmetric rotor and the effects of centrifugal distortion were described by the Watson A-reduced Hamiltonian in the I^R representation. It was found that only two of the quartic centrifugal distortion constants, namely, Δ_J and Δ_{JK} , were determinable from the observed transitions and therefore Δ_K , δ_J , and δ_K were held fixed at the values obtained from the DFT calculation at the B3LYP/6-311++(3df,2pd) level. The observed transition frequencies and the residual differences $\Delta\nu$ between the observed and calculated frequencies are in the Supporting Information, Table 4S, while the spectroscopic constants obtained from the fit are given in Table 3. The comparatively large error associated with the rotational constant A_0 can be attributed to the failure to detect either μ_b or μ_c transitions, since the observed a-type transitions do not depend on A_0 to a large extent and therefore this

TABLE 3: Experimentally Determined Spectroscopic Constants for Three Conformers of Cyclopropylmethylphosphine

spectroscopic constant	conformer		
	III	IV	V
<i>A</i> /MHz	10878.235(17)	10959.4(32)	10784.640(9)
<i>B</i> /MHz	1984.7682(19)	1945.130(9)	2000.0835(16)
<i>C</i> /MHz	1831.6144(18)	1804.566(9)	1846.6393(16)
Δ_J /kHz	0.650(5)	0.536(8)	0.772(3)
Δ_{JK} /kHz	-4.32(4)	-3.29(9)	-5.272(9)
Δ_K /kHz	25.98(24)	26.1 ^a	30.6(5)
δ_J /kHz	0.1003(3)	0.07 ^a	0.11613(8)
δ_K /kHz	2.09(13)	1.9 ^a	2.52(2)
ϕ_J /kHz	0.00017(3)		
ϕ_{JK} /kHz			0.109(6)
σ /kHz	0.15	0.23	0.14
<i>N</i>	123	114	161

^a Fixed at value obtained from B3LYP/6-311++(3df,2pd) density functional calculation.

parameter cannot be precisely determined by an analysis of μ_a transitions alone.

Having established a satisfactory assignment of the a-type spectrum of conformer IV, an attempt was made to assign the rotational spectra of vibrationally excited states by means of the radio frequency microwave double-resonance (RFMWDR) technique. Transitions attributable to five vibrationally excited states were assigned and the least-squares analysis of these transitions yielded the spectroscopic constants presented in Table 4 (spectra in Supporting Information Tables 5S–9S). The states labeled IVa, IVb, and IVc in Table 4 are believed to be the first, second and third excited states of a single mode of vibration. A calculation of the vibrational frequencies performed for conformer IV at the B3LYP/6-311++(3df,2pd) level predicted that the torsional motion about the C1–C2 bond would be the lowest in energy (94.1 cm⁻¹), so it is considered likely that states IVa, IVb, and IVc correspond to this motion. The states given as IVd and IVe are likely to be the first excited states of the torsional motion of the -PH₂ group and the lowest energy bending vibration, which are predicted to occur at 174.7 and 195.1 cm⁻¹, respectively. An exact assignment of states IVd and IVe to one or other of these two modes is not possible from the available spectral data, since both display transitions of similar intensity, displaced by a small shift in frequency from transitions in the ground-state rotational spectrum.

Assignment of Conformer III. A prediction for the rotational spectrum of conformer III was made by evaluating the differences between the experimental ground-state rotational constants of conformer IV and the equilibrium constants obtained for this conformer from an ab initio calculation at the MP2/6-311++G(3df,2pd) level. These differences were then applied as a correction to the rotational constants calculated at

TABLE 4: Experimentally Determined Spectroscopic Constants for Vibrationally Excited States of Two Conformers of Cyclopropylmethylphosphine

spectroscopic constant	state						
	IIIa	IIIb	IVa	IVb	IVc	IVd	IVe
A/MHz	10 878 ^a	10 878 ^a	10 950.2(39)	10 957(26)	10 959 ^a	10 959 ^a	10 959 ^a
B/MHz	1982.243(17)	1985.57(10)	1940.700(11)	1937.397(18)	1934.001(24)	1944.961(53)	1944.36(19)
C/MHz	1830.427(19)	1832.72(12)	1802.125(11)	1800.505(16)	1798.890(32)	1803.611(57)	1803.08(20)
Δ_J /kHz	0.6 ^b	0.6 ^b	0.533(9)	0.557(18)	0.556(17)	0.5 ^b	0.5 ^b
Δ_{JK} /kHz	-4.4 ^b	-4.4 ^b	-3.3 ^b	-2.10(25)	-2.46(34)	-6.67(43)	-1.40(66)
Δ_K /kHz	29.2 ^b	29.2 ^b	26.1 ^b	26.1 ^b	26.1 ^b	26.1 ^b	26.1 ^b
δ_J /kHz	0.1 ^b	0.1 ^b	0.07 ^b	0.07 ^b	0.07 ^b	0.07 ^b	0.07 ^b
δ_K /kHz	2.3 ^b	2.3 ^b	1.9 ^b	1.9 ^b	1.9 ^b	1.9 ^b	1.9 ^b
σ /kHz	0.22	0.21	0.25	0.22	0.29	0.09	0.09
N	24	18	83	37	27	13	8

^a Fixed at experimental value obtained for ground-state species. ^b Fixed at value obtained from B3LYP/6-311++(3df,2pd) density functional calculation.

the same level of theory for conformer III. Using these corrected rotational constants in conjunction with a set of quartic centrifugal distortion constants from a DFT calculation performed at the B3LYP/6-311++G(3df,3pd) level enabled a prediction of the spectrum of conformer III to be evaluated. This prediction allowed the characteristic a-type, R-branch transitions of this conformer to be readily assigned. The DFT calculation undertaken for this conformer predicted that the components of the electric dipole moment would be $\mu_a = 0.93$ D, $\mu_b = -0.45$ D, and $\mu_c = 0.63$ D. Therefore, having fitted the a-type, R-branch transitions in a least-squares analysis, as described above, it was possible to predict the frequencies of the c-type transitions to within a few megahertz. A number of these transitions were subsequently identified and included in the fit, leading to a significant improvement in the error associated with the rotational constant A_0 , as expected. No b-type transitions were observed for this conformer, despite the fact that μ_b was estimated to be -0.45 D by the DFT calculations performed for this conformer. It should be noted, however, that the assignment of both a- and c-type rotational transitions enabled the frequencies of the b-type transitions to be predicted with a high degree of accuracy. The failure to observe b-type transitions suggests that the value of μ_b given by the DFT calculation represents an overestimate in this case.

Experimental measurements of transition frequencies and residual errors for conformer III are included in Supporting Information, Table 1S, while the spectroscopic constants obtained from the least-squares analysis of this conformer are reported in Table 3. It was found that all five of the quartic centrifugal distortion constants, together with the sextic distortion constant φ_J , were required to give a satisfactory error in the fit.

Rotational spectra belonging to two vibrationally excited states were assigned with the aid of the RFMWDR technique. The spectroscopic constants obtained by fitting these spectra are included in Table 4 (spectra are given in Supporting Information Tables 2S and 3S). A calculation of the vibrational frequencies of conformer III conducted at the B3LYP/6-311++G(3df,2pd) level of theory predicted that the lowest energy vibrations would be the torsional motion about the C1–C2 bond (90.3 cm⁻¹), the torsional motion of the -PH₂ group (150.2 cm⁻¹), and the lowest energy bending vibration (191.7 cm⁻¹), as was the case for conformer IV. The state labeled IIIa in Table 4 was attributed to the torsion about the C1–C2 bond and it is assumed that state IIIb corresponds to either the torsion of the -PH₂ group or the lowest energy bending mode, but a definitive assignment is not possible from the available data.

Assignment of Conformer V. An accurate prediction of the spectrum of conformer V was made by employing a similar

correction to that previously used for conformer III. Use of this prediction allowed the assignment of a weak a-type spectrum and a richer b-type spectrum. This is consistent with an estimate of the electric dipole moment components at the B3LYP/6-311++G(3df,2pd) level, which gave $\mu_a = -0.77$ D, $\mu_b = -0.93$ D, and $\mu_c = 0.19$ D. The observed transition frequencies and residual errors from the least-squares fit of this conformer are included in Supporting Information Table 10S, and the spectroscopic constants obtained from the fit are given in Table 3. It was found that the five quartic centrifugal distortion constants and the sextic distortion constant φ_{JK} were required to give a satisfactory quality of fit.

It was not possible to identify any transitions belonging to vibrationally excited states of this conformer when either the standard mode of operation or the RFMWDR technique was used.

Failure to Detect Conformers I and II. No transitions were identified that could be attributed to either conformer I or II, despite having used the RFMWDR method to perform careful searches of the frequency ranges in which transitions were predicted by use of spectroscopic constants obtained from quantum chemical calculations.

Relative Intensity Measurements. Approximate values for the relative energies of the three conformers of cyclopropylmethylphosphine observed spectroscopically were determined by comparing the intensities of selected ground-state transitions,²⁰ with the assumption of a Boltzmann distribution among the conformers, and using the values of the dipole moments obtained from the B3LYP/6-311++G(3df,2pd) geometry optimizations. In this way, conformer IV was found to be the lowest in energy, with conformer III being higher in energy by 1.7 kJ mol⁻¹ and conformer V higher than IV by 2.4 kJ mol⁻¹. It can be seen from Table 2 that these values are in good agreement with the findings of the ab initio study conducted on this molecule.

A comparison of relative transition intensities was also used to estimate the energy difference between the vibrationally excited state IVa, believed to correspond to the $\nu = 1$ level of the torsion about the C1–C2 bond, and the vibrational ground state of conformer IV. A Boltzmann energy distribution was assumed once more, and by comparing a number of transitions belonging to both states, a value of 80.1 cm⁻¹ was obtained, which compares favorably with an estimate of 94.1 cm⁻¹ predicted for this mode from the aforementioned DFT calculation. A similar treatment for state IIIa yielded a value of 114.7 cm⁻¹ for the $\nu = 0 \leftarrow 1$ transition, as compared to 114.7 cm⁻¹ from the DFT calculation. Owing to the inaccuracies inherent in the determination of relative intensities, the error associated

TABLE 5: Geometries^a of Three Conformers of Cyclopropylmethylphosphine from ab Initio Calculations at the MP2/Aug-cc-pVTZ Level of Theory

molecular dimension	conformer		
	III	IV	V
Bond Lengths			
$r(\text{P}-\text{H}_1)$	141.4	141.5	141.5
$r(\text{P}-\text{H}_2)$	141.5	141.5	141.5
$r(\text{P}-\text{C}_1)$	186.6	186.3	186.7
$r(\text{C}_1-\text{H}_3)$	109.2	109.3	109.0
$r(\text{C}_1-\text{H}_4)$	109.1	109.4	109.3
$r(\text{C}_1-\text{C}_2)$	150.5	150.3	150.5
$r(\text{C}_2-\text{H}_5)$	108.3	108.3	108.3
$r(\text{C}_2-\text{C}_3)$	150.5	150.6	150.6
$r(\text{C}_2-\text{C}_4)$	150.5	150.3	150.4
$r(\text{C}_3-\text{H}_6)$	108.8	108.0	108.0
$r(\text{C}_3-\text{H}_7)$	108.8	108.1	108.1
$r(\text{C}_3-\text{C}_4)$	150.9	151.0	150.9
$r(\text{C}_4-\text{H}_8)$	107.9	107.9	107.9
$r(\text{C}_4-\text{H}_9)$	108.1	108.1	108.1
Bond Angles			
$\angle(\text{H}_1, \text{P}, \text{C}_1)$	96.9	96.7	97.9
$\angle(\text{H}_2, \text{P}, \text{C}_1)$	97.9	96.7	96.6
$\angle(\text{P}_1, \text{C}_1, \text{C}_2)$	109.8	115.4	109.9
$\angle(\text{H}_3, \text{C}_1, \text{C}_2)$	110.6	111.2	111.2
$\angle(\text{H}_4, \text{C}_1, \text{C}_2)$	109.9	109.9	109.3
$\angle(\text{C}_1, \text{C}_2, \text{C}_3)$	119.5	119.6	119.6
$\angle(\text{C}_1, \text{C}_2, \text{C}_4)$	118.6	118.8	118.8
$\angle(\text{H}_5, \text{C}_2, \text{C}_1)$	115.4	115.2	115.3
$\angle(\text{H}_6, \text{C}_3, \text{C}_2)$	118.2	118.4	118.2
$\angle(\text{H}_7, \text{C}_3, \text{C}_2)$	117.0	117.0	116.9
$\angle(\text{H}_8, \text{C}_4, \text{C}_2)$	118.6	118.6	118.5
$\angle(\text{H}_9, \text{C}_4, \text{C}_2)$	116.7	116.8	116.6
Dihedral Angles			
$\angle(\text{H}_1, \text{P}-\text{C}_1, \text{C}_2)$	-74.0	48.3	163.9
$\angle(\text{H}_2, \text{P}-\text{C}_1, \text{C}_2)$	-168.9	-46.0	69.5
$\angle(\text{P}, \text{C}_1-\text{C}_2, \text{C}_3)$	154.6	153.8	148.7
$\angle(\text{P}, \text{C}_1-\text{C}_2, \text{C}_4)$	84.8	83.6	78.6
$\angle(\text{H}_3, \text{C}_1-\text{C}_2, \text{C}_3)$	-86.9	-84.3	-87.4
$\angle(\text{H}_4, \text{C}_1-\text{C}_2, \text{C}_4)$	-37.8	-37.0	-38.5
$\angle(\text{H}_5, \text{C}_2-\text{C}_1, \text{P})$	-59.3	-60.5	-65.7
$\angle(\text{H}_6, \text{C}_3-\text{C}_2, \text{C}_1)$	144.4	144.1	144.1
$\angle(\text{H}_7, \text{C}_3-\text{C}_2, \text{C}_1)$	-0.4	-0.9	-0.5
$\angle(\text{H}_8, \text{C}_3-\text{C}_2, \text{C}_1)$	-142.9	-142.9	-142.8
$\angle(\text{H}_9, \text{C}_3-\text{C}_2, \text{C}_1)$	2.0	1.9	1.6

^a Distances are given in picometers and angles are given in degrees.

with these experimentally derived values is estimated to be on the order of 15–20 cm^{-1} .

Stark-Effect Measurements. It was not possible to make a quantitative measurement of the dipole moment of any conformer of cyclopropylmethylphosphine by means of the Stark effect, as the low- J transitions used in such measurements lacked sufficient intensity.

Intramolecular Hydrogen Bonding

The close agreement between the experimentally determined rotational constants and those obtained from ab initio calculations at the MP2/aug-cc-pVTZ level of theory suggests that the structures yielded by these calculations represent a good approximation of the molecular geometries. The approximate r_e structures obtained from the ab initio calculations performed at this level of theory for conformers III, IV, and V are presented in Table 5, while structures obtained by the same method for conformers I and II are given in Supporting Information, Table 11S. A careful analysis of these structures was undertaken, with particular attention being paid to the distance between the H-atoms of the PH_2 group and the midpoint of the C2–C3 bond.

The possible interaction between one of the phosphine H-atoms and the electron density associated with the so-called banana bonds along the edges of the cyclopropyl ring would represent the formation of an intramolecular hydrogen bond. It was, however, difficult to find convincing evidence of a close approach between a phosphine H-atom and the midpoint of the C2–C3 bond in the two synclinal (obsolete gauche) conformers (namely, conformers III and IV) in which hydrogen-bond formation might occur. The distance associated with this parameter was found to be 304 pm for conformer III and 288 pm in the case of conformer IV, which is not considered to be significantly different from that expected from the sum of the van der Waals radii of the groups involved (~ 290 pm).²¹ Equally, the consistency of the bond lengths $r(\text{P}-\text{H}_1)$ and $r(\text{P}-\text{H}_2)$ from the MP2/aug-cc-pVTZ calculations for conformers III–V suggests that if an internal hydrogen bond is formed in either conformer III or IV, then the magnitude of this bonding interaction must be very small.

Weak evidence in favor of the stabilization of this molecule by intramolecular hydrogen bonding is provided by the fact that out of three conformers whose microwave spectra were recorded, the two most stable conformers were those in which the cyclopropyl banana bonds and a phosphine H-atom may approach and interact, which is not possible for conformer V. This may, however, be purely coincidental and is far from conclusive evidence in any case.

Conclusions

The microwave spectrum of cyclopropylmethylphosphine was recorded in the 12–62 GHz frequency range by means of Stark-modulation microwave spectroscopy. Transitions observed in this spectrum could be assigned to the three gauche forms possible for this molecule. The rotational spectra of seven vibrationally excited states of the molecule were also observed and a number of these were tentatively assigned with the aid of DFT calculations.

It was found that equilibrium structures obtained from ab initio geometry optimizations performed for the three gauche conformers at the MP2/aug-cc-pVTZ level of theory had equilibrium rotational constants with values very similar to the experimental, ground-state rotational constants of the corresponding conformers. The differences were typically on the order of 1%, which represents a close agreement between experiment and theory, even when the minor differences between r_0 and r_e structures are considered.

The relative energies of the three observed conformers were also evaluated by comparing the intensities of rotational transitions and by G3 quantum chemical calculations. There was found to be good agreement between the calculated and experimentally derived values of the relative energies of these three conformers.

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Supporting Information Available: Assigned microwave spectra and additional results from quantum chemical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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