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Synthesis and Microwave Spectrum of (2-Chloroethyl)phosphine ($ClCH_2CH_2PH_2$)

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The synthesis of a 2-halogenoethylphosphine, (2-chloroethyl)phosphine ($ClCH_2CH_2PH_2$), is reported for the first time. This compound was prepared by a chemoselective reduction of diethylchloroethylphosphonate with dichloroalane using a vacuum line. (2-Chloroethyl)phosphine has been studied by microwave spectroscopy at room temperature, or at −20 °C, in the 22−80 GHz spectral interval. The experimental study has been augmented by quantum chemical calculations at the MP2/6-311++(3df,3pd) and B3LYP/6-311++(3df,3pd) levels of theory. The spectra of two rotameric forms, denoted **I** and **II** have been assigned. These conformers both have an antiperiplanar arrangement for the Cl−C−C−P chain of atoms, but with different orientation of the phosphine group. Conformer **I** was found to be 5.2(6) kJ/mol more stable than **II** by relative intensity measurements. The spectra of the first excited states of the C−C torsional vibration of both **I** and **II** were assigned. The torsional frequency was determined to be 63(20) cm^{-1} for conformer **I** by relative intensity measurements, and it has a similar value in **II**. It was found that this normal vibration deviates from a near-harmonic behavior. The quantum chemical calculations produce rotational and centrifugal distortion constants that are in satisfactory agreement with observations, but fail to predict correctly low-frequency fundamental frequencies. The quantum chemical calculations indicate that three additional conformers characterized by a synclinal orientation for the Cl−C−C−P link of atoms and with different orientation of the phosphine group are high-energy forms of $ClCH_2CH_2PH_2$. Searches for these forms were unsuccessful.

Introduction

Relatively few experimental studies of the structural and conformational properties of gaseous aliphatic phosphines have been reported, presumably because of their toxicity, obnoxious smells, and instability toward air. Microwave (MW) spectroscopy has been employed to investigate CH_3PH_2,[1] $(CH_3)_2PH$,[2,3] $(CH_3)_3CPH_2$,[4] $(CH_3)_3P$,[5] $(CH_3)_2CHPH_2$,[6] $CH_3CH_2PH_2$,[7,8] cyclopropylphosphine ($C_3H_5PH_2$),[9] $H_2PCH_2CH_2C{\equiv}N$,[10] $HC{\equiv}CPH_2$,[11] $H_2C{=}CHPH_2$,[12,13] $H_2PCH_2CH_2PH_2$,[14] $HC{\equiv}CCH_2PH_2$,[15] $H_2C{=}CHCH_2PH_2$,[16] $H_2C{=}C{=}CHPH_2$,[17] phosphirane (C_2H_5P),[18] (cyclopropylmethyl)phosphine ($C_3H_5CH_2PH_2$),[19] and cyclopentadienylphosphine ($C_5H_5PH_2$).[20] These studies have revealed that phosphines have unique structural and conformational properties. It has also been shown that the gas phase may contain a complex mixture of several rotameric forms of some of these phosphines. Conformational equilibria have, for example, been demonstrated to exist for $CH_3CH_2PH_2$,[7,8] $H_2PCH_2CH_2C{\equiv}N$,[10] $H_2PCH_2CH_2PH_2$,[14] $H_2C{=}CHCH_2PH_2$,[16] $H_2C{=}C{=}CHPH_2$,[17] $C_3H_5CH_2PH_2$,[19] and $C_5H_5PH_2$.[20]

No halogenated phosphines, such as title compound (2-chloroethyl)phosphine ($ClCH_2CH_2PH_2$), appear to have been investigated by MW spectroscopy in the past. It was thought that it would be of interest to investigate this compound to see what conformational consequences introduction of the electronegative chlorine atom (Pauling electronegativity of 3.16) in the 2-position of ethylphosphine would have. However, a literature survey revealed that the synthesis of $ClCH_2CH_2PH_2$ had not been reported previously. It was therefore decided to synthesize this compound and to study its conformational properties by MW spectroscopy augmented with high-level quantum chemical calculations.

Five rotameric forms can be envisaged for the $ClCH_2CH_2PH_2$. These five forms with atom numbering are shown in Figure 1. The Cl−C−C−P chain of atoms is antiperiplanar in rotamers **I** and **II**, and synclinal in the remaining three conformers. The C−C−P−H links are + and − synclinal, respectively, in **I** and **III**. One of these chains is antiperiplanar, and the other is + or − synclinal in **II**, **IV**, and **V**.

A successful investigation of a delicate conformational equilibrium such as the one presented by (2-chloroethyl)phosphine requires experimental methods possessing high resolution. MW spectroscopy meets this requirement because of its superior accuracy and resolution, making this method especially well suited for conformational studies of gaseous species. The spectroscopic work has been augmented by high-level quantum chemical calculations, which were conducted with the purpose of obtaining information for use in assigning the MW spectrum and investigating properties of the potential-energy hypersurface.

Experimental Section

Caution. *(2-Chloroethyl)phosphine is malodorous, pyrophoric, and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.*

Synthesis. We have prepared the novel compound (2-chloroethyl)phosphine by a chemoselective reduction of diethyl (chloroethyl)phosphonate with dichloroalane in a vacuum line.

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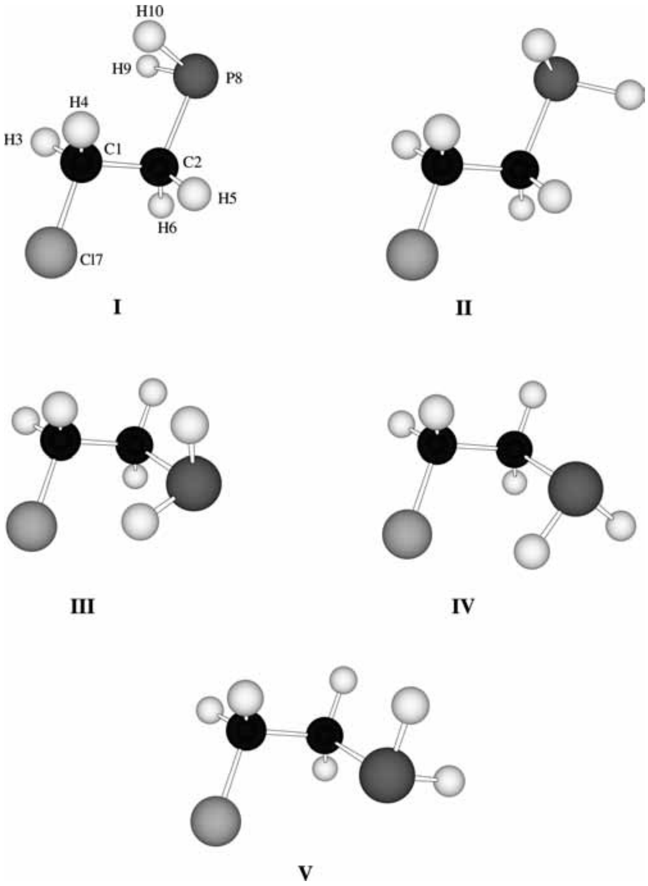

Figure 1. Model of $ClCH_2CH_2PH_2$ with atom numbering. The MW spectra of conformers **I** and **II** were assigned. **I** was found to be 5.2(6) kJ/mol more stable than **II** by relative intensity measurements. MP2 and B3LYP calculations predict **I** to be favored by ~5−12 kJ/mol relative to the other rotamers.

(2-Chloroethyl)phosphine. (Chloroethyl)phosphonic acid diethyl ester was purchased from the ACROS Co. and used without further purification.

$LiAlH_4$ (0.76 g, 20 mmol) and dry tetraglyme (50 mL) were introduced into a 250 mL two-necked flask equipped with a stirring bar and a nitrogen inlet. The flask was immersed in a cold bath (−30 °C), and aluminum chloride (8.0 g, 60 mmol) was added in portions. The flask was attached to a vacuum line equipped with two traps with stopcocks and evacuated. The reaction mixture was allowed to warm to −10 °C and stirred for 5 min. (2-Chloroethyl)phosphonic acid diethyl ester (2.01 g, 10 mmol) diluted in tetraglyme (10 mL) was slowly introduced into the reaction mixture. The (chloroethyl)phosphine was evacuated from the reaction mixture as it was formed. High-boiling impurities were removed in the first trap cooled at −60 °C and the phosphine was selectively trapped in the second trap cooled to −110 °C. Yield: 0.704 g, 7.3 mmol, 73%. The pure compound can be kept for months in a Schlenk flask at −20 °C. ^{1}H NMR ($CDCl_3$): δ 1.97 (m, 2H, $^2J_{PH} = 8.0$ Hz, $^3J_{HH} =$ 6.6 Hz, $CH_2{-}P$), 2.70 (dm, 2H, $^1J_{PH} = 196.1$ Hz, PH_2), 3.53 (AB system, 2H, $^3J_{PH} = 4.6$ Hz, CH_2Cl). ^{13}C NMR ($CDCl_3$): δ 18.4 (t, $^1J_{CH} = 132.7$ Hz, $^1J_{PC} = 13.8$ Hz (d), CH_2P), 46.2 (t, $^1J_{CH} = 152.6$ Hz, $^2J_{PC} = 2.9$ Hz (d), CH_2Cl). ^{31}P NMR ($CDCl_3$): δ −146.7 (t). IR (ν, cm^{-1}, gas phase, 60 mbar): 723 (s), 1049 (m), 1130 (s), 1295 (s), 2302 (s, ν_{PH}), 2886 (m), 2964 (m). HRMS: calcd for C_2H_6ClP, 95.9896; found, 95.990.

Microwave Experiment. The spectrum of (2-chloroethyl)phosphine was studied in the 22−80 GHz frequency interval by Stark-modulation spectroscopy using the microwave spectrometer of the University of Oslo. Details of the construction and operation of this device have been given elsewhere.[20,21] This spectrometer has a resolution of about 0.5 MHz and measures the frequency of isolated transitions with an estimated accuracy of ≈0.10 MHz. The experiments were performed at room temperature, or at about −20 °C, at a pressure of roughly 10 Pa.

Quantum Chemical Methods. The present ab initio and density functional theory (DFT) calculations were performed employing the Gaussian 03 suite of programs,[22] running on the Titan cluster in Oslo. Electron correlation was taken into consideration in the ab initio calculations using Møller−Plesset second-order perturbation calculations (MP2).[23] Becke's three-parameter hybrid functional[24] employing the Lee, Yang, and Parr correlation functional (B3LYP)[25] was employed in the DFT calculations. The 6-311++G(3df,3pd) wave function, which is of triple-ζ quality and augmented with diffuse functions, were used in both MP2 and B3LYP calculations. Geometry optimizations with no symmetry restraints were performed on the five possible rotameric forms of (2-chloroethyl)phosphine shown in Figure 1 employing the default convergence criteria of Gaussian 03.

Results and Discussion

Quantum Chemical Calculations. The energies, structures, rotational and centrifugal distortion constants, and dipole moments were calculated for conformers **I**−**V** employing both the MP2 and B3LYP procedures. Calculations of the vibration−rotation constants (the α's)[26] were undertaken using the B3LYP procedure, because MP2 calculations with the 611++G(3df,3pd) are too expensive. The MP2 structures are shown in Table 1, while the corresponding B3LYP structures are collected in Table 1S in the Supporting Information. No imaginary vibrational frequencies were calculated for any of the five rotamers, implying that these forms are minima on the potential energy hypersurface.

The rotational constants calculated from the MP2 structures are shown in Table 2, together with Watson's *A*-reduction quartic centrifugal distortion constants,[27] the components of the dipole moment along the principal inertial axes, and the energy differences relative to the energy of the global minimum conformer, which turned out to be **I**. The energy differences have been corrected for zero-point vibrational energies. Corresponding B3LYP parameters are listed in the Supporting Information, Table 2S.

Both the MP2 (Table 2) and B3LYP (Table 2S, Supporting Information) calculations predict that **I** is the preferred form of the molecule by ~5−12 kJ/mol relative to the four other forms. The calculated energy differences show the same trends in both calculation procedures.

There are some noteworthy differences in the structures calculated by these two methods, particularly associated with the C1−Cl7 and C2−P8 bonds. The B3LYP C1−Cl7 bond lengths of the five conformers (Table 1S, Supporting Information) are roughly 3 pm longer than the corresponding MP2 bond lengths (Table 1). The equilibrium (r_e) bond length of the C−Cl bond length in CH_3CH_2Cl has been estimated to be 178.9(2) pm.[28] This value is close to the MP2 predictions (Table 1) for the five forms (178.0−178.6 pm).

The MP2 C2−P8 bond lengths are predicted to be about 1.5 pm shorter than their B3LYP counterparts (Tables 1 and 1S (Supporting Information)). An r_e value of 185.29(1) pm for this bond length has been reported[29] for a conformer of $H_3CCH_2PH_2$ similar to **I**, whereas r_e = 184.91(3) pm was found for a

TABLE 1: MP2/6-311++(3df,3pd) Structures of Five Conformers of $ClCH_2CH_2PH_2$

	I[a]	II[a]	III	IV	V
		Bond Length (pm)			
C1–C2	**151.1**	**151.4**	151.7	151.6	151.7
C1–H3	**108.7**	**108.7**	108.7	108.7	108.8
C1–H4	**108.7**	**108.7**	108.7	108.7	108.7
C1–Cl7	**178.6**	**178.2**	178.0	178.2	178.0
C2–H5	**109.0**	**109.0**	109.3	109.2	109.0
C2–H6	**109.0**	**108.7**	109.1	108.8	109.0
C2–P8	**185.3**	**186.1**	185.2	185.9	186.2
P8–H9	**141.1**	**140.8**	140.7	140.9	141.2
P8–H10	**141.1**	**141.0**	141.1	140.7	141.0
		Angles (deg)			
C2–C1–H3	**111.3**	**111.5**	111.3	111.3	111.4
C2–C1–H4	**111.3**	**111.4**	110.9	111.4	110.9
C2–C1–Cl7	**111.3**	**111.1**	112.1	111.3	112.0
H3–C1–H4	**109.1**	**109.0**	109.2	109.4	108.9
H3–C1–Cl7	**106.8**	**106.6**	107.0	106.7	106.9
H4–C1–Cl7	**106.8**	**106.9**	106.2	106.6	106.6
C1–C2–H5	**110.2**	**109.4**	108.0	107.7	108.0
C1–C2–H6	**110.2**	**110.2**	109.8	110.2	109.3
C1–C2–P8	**114.0**	**109.5**	117.5	111.9	112.5
H5–C2–H6	**107.0**	**108.2**	106.7	108.1	108.1
H5–C2–P8	**107.6**	**107.5**	106.5	106.6	110.9
H6–C2–P8	**107.6**	**112.0**	107.8	112.2	107.9
C2–P8–H9	**97.0**	**96.8**	97.4	96.3	95.9
C2–P8–H10	**97.0**	**97.0**	96.5	98.2	96.0
H9–P8–H10	**93.6**	**93.8**	93.8	94.0	93.3
		Dihedral Angle (deg)			
H3–C1–C2–H5	**–177.9**	**–178.9**	68.4	62.8	64.7
H3–C1–C2–H6	**–60.1**	**–60.0**	–175.7	–179.6	–177.9
H3–C1–C2–P8	**61.0**	**63.6**	–52.0	–54.1	–58.0
H4–C1–C2–H5	**60.1**	**59.1**	–53.4	–59.6	–56.8
H4–C1–C2–H6	**177.9**	**177.9**	62.5	58.1	60.7
H4–C1–C2–P8	**–61.0**	**–58.4**	–173.8	–176.4	–179.5
Cl7–C1–C2–H5	**–58.9**	**–60.1**	–171.9	–178.3	–175.7
Cl7–C1–C2–H6	**58.9**	**58.8**	–55.9	–60.7	–58.3
Cl7–C1–C2–P8	**180.0**	**–177.6**	67.7	64.8	61.6
C1–C2–P8–H9	**–47.3**	**–171.6**	–47.8	178.8	68.2
C1–C2–P8–H10	**47.2**	**–76.9**	47.0	–86.2	162.2
H5–C2–P8–H9	**–169.8**	**69.7**	–169.0	61.3	–52.9
H5–C2–P8–H10	**–75.3**	**164.4**	–74.3	156.3	41.1
H6–C2–P8–H9	**75.3**	**–49.1**	76.8	–56.8	–171.1
H6–C2–P8–H10	**169.8**	**45.6**	171.6	38.2	–77.1

[a] The MW spectra of these conformers were assigned.

conformer similar to **II**.[29] These values are much closer to the MP2 predictions (185.2−186.2 pm; Table 1) than to the B3LYP results (186.7−187.8 pm; Table 1S, Supporting Information). Both methods predict the bond angles to agree to within better than ∼1.5°, and the dihedral angles to deviate by less than roughly 2°.

The quartic centrifugal distortion constants predicted by the two methods vary somewhat (Table 2 and 2S (Supporting Information)). This is not surprising since they depend on the second derivative at the minima of the potential energy hypersurface. The B3LYP dipole moments (same tables) are generally somewhat smaller than their MP2 counterparts, which is typical.

TABLE 2: MP2/6-311++G(3df,3pd) Parameters of Spectroscopic Interest of Five Conformers[a] of $^{35}ClCH_2CH_2PH_2$

	I[b]	II[b]	III	IV	V
		Rotational Constants (MHz)			
A	**24559.4**	**24769.1**	9345.6	8948.5	8997.2
B	**1460.0**	**1469.4**	2153.0	2292.1	2264.4
C	**1418.7**	**1425.9**	1878.4	1955.2	1945.1
		Quartic Centrifugal Distortion Constants[c] (kHz)			
Δ_J	**0.135**	**0.149**	1.09	1.79	2.06
Δ_{JK}	**–1.34**	**–1.72**	–8.57	–12.6	–16.2
Δ_K	**57.2**	**63.3**	37.9	40.2	54.6
δ_J	**0.00538**	**0.00640**	0.249	0.452	0.541
δ_K	**–0.0148**	**0.0656**	2.72	3.73	4.56
		Dipole Moment (10^{-30} C m)			
μ_a	**3.78**	**4.77**	0.82	2.59	3.56
μ_b	**2.81**	**0.37**	6.50	7.25	8.88
μ_c	**0.00**[d]	**1.86**	2.05	1.80	1.41
		Energy Difference[e] (kJ/mol)			
ΔE	**0.0**	**5.9**	4.7	6.0	9.7

[a] Minima on the potential energy hypersurface; see text. [b] The MW spectra of these conformers were assigned. [c] *A*-reduction.[27] [d] For symmetry reasons. [e] Relative to conformer **I** and corrected for the zero-point energy. Electronic energy of conformer **I**: −2 311 002.08 kJ/mol.

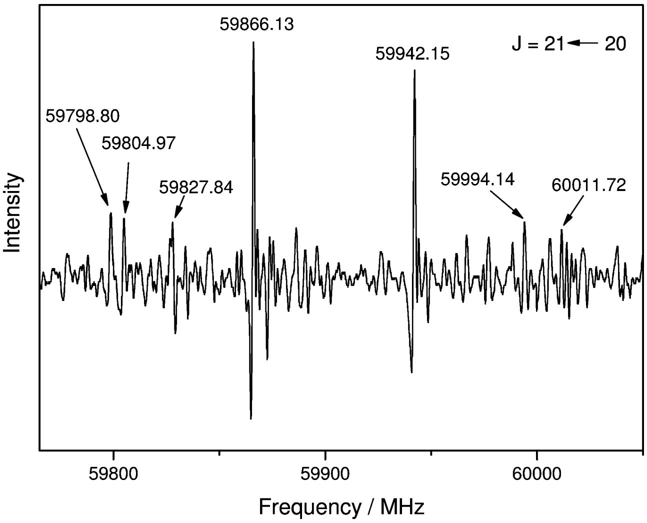

Figure 2. ^aR $J = 21 \leftarrow 20$ pile-up region of conformer **I** of $ClCH_2CH_2PH_2$. This spectrum was taken with a Stark modulation field strength of approximately 110 V/cm. The frequencies of band heads are indicated.

Microwave Spectrum and Assignment of Conformer I of $ClCH_2CH_2PH_2$. This rotamer is predicted to be the preferred form of the molecule by ∼5 kJ/mol relative to the other conformers in both the MP2 and B3LYP calculations (Tables 2 and 2S (Supporting Information)). There are two naturally occurring isotopes of chlorine, namely, ^{35}Cl (75.5%) and ^{37}Cl (24.5%). Both isotopologues of **I** are nearly prolate rotors (Ray's asymmetry parameter[30] $\kappa \sim -0.996$ in each case), with μ_a as their major dipole moment component (Tables 2 and 2S (Supporting Information)). Pile-ups of ^aR-branch transitions separated by approximately $B + C \sim 2.88$ GHz (Table 2) for the ^{35}Cl isotopologue were therefore expected to occur, whereas the structure in Table 1 yields $B + C \sim 2.81$ GHz for the ^{37}Cl species.

Survey spectra revealed series of comparatively strong ^aR pile-ups close to their predicted frequencies. The $J = 21 \leftarrow 20$ pile up of $^{35}ClCH_2CH_2PH_2$ shown in Figure 2 is a typical example. It should be evident from this figure that the pile-ups have a complicated fine structure caused by the spectra of the ground and of vibrationally excited states. Relatively few and weak spectral lines were seen in the spectral intervals between the pile-ups.

Pairs of ^aR-lines with identical $K_{-1} \geq 4$ coalesce, because $\kappa \sim -1$. These transitions are modulated at relatively low Stark

TABLE 3: Spectroscopic Constants[a] of the Ground Vibrational States of the $^{35}ClCH_2CH_2PH_2$ and $^{37}ClCH_2CH_2PH_2$ Isotopologues of Conformer I

species:	$^{35}ClCH_2CH_2PH_2$[b]	$^{37}ClCH_2CH_2PH_2$[c]
A (MHz)	24287(16)	24228(15)
B (MHz)	1445.8842(23)	1408.7714(33)
C (MHz)	1404.8867(25)	1369.7870(40)
Δ_J (kHz)	0.1385(13)	0.1356(12)
Δ_{JK} (kHz)	−1.44(4)	−1.45(7)
Δ_K (kHz)	57.2[d]	57.2[d]
δ_J (kHz)	0.00538[d]	0.00538[d]
δ_K (kHz)	−0.0148[d]	−0.0148[d]
rms[e]	1.078	0.920
no. of transitions[f]	153	72
$I_c - I_a - I_b$[g] (10^{-20} u m^2)	−10.61(1)	−10.65(1)

[a] A-Reduction I^r-representation.[27] Uncertainties represent one standard deviation. [b] The spectrum is listed in Table 3S, Supporting Information. [c] The spectrum is listed in Table 5S, Supporting Information. [d] Fixed, see text. [e] Root-mean-square deviation of a weighted fit. [f] Number of transitions used in the least-squares fit. [g] Principal moments of inertia. Conversion factor: 505 379.05 MHz 10^{-20} u m^2.

fields, which facilitated their assignments. The MP2 values of the Δ_J and Δ_{JK} centrifugal distortion constants were also useful in this respect. A typical feature of the spectrum of this conformer is the fact that several of the strongest K_{-1} pairs overlap producing a comparatively strong "band head". An example is the absorption at 59 866.13 MHz in Figure 2.

The ^{35}Cl and ^{37}Cl nuclei have spins = $^3/_2$ and a quadrupole hyperfine structure therefore results from coupling of the nuclear spin with the overall rotation of the molecule. However, these splittings were not expected to be large enough to produce a resolvable fine structure of the $J \geq 9$ ^aR-lines that were assigned in the present case. However, the observed MW lines were comparatively broad but not split.

A total of 153 ^aR-transitions with $9 \leq J \leq 28$ were ultimately assigned and fitted employing Watson's A-reduction Hamiltonian with the I^r-representation,[27] using Sørensen's program Rotfit.[31] b- and c-type lines were searched for, but not found, presumably because the corresponding dipole moment components are smaller than μ_a (Table 2). Quadrupole splitting caused by the chlorine atom is much more significant for these kind of transitions than for the ^aR-transitions. This effect would reduce the intensities further making a safe assignment of b- and c-type lines even more difficult. The spectrum of the ^{35}Cl isotopologue is shown in Table 3S in the Supporting Information and the spectroscopic constants are listed in Table 3. The uncertainties given in Table 3S were used as weights in the least-squares fit.

The assigned ^aR-lines furnish insufficient information for an accurate determination of the A rotational constant, whose one standard deviation is 16 MHz (Table 3). The quartic centrifugal distortion constants Δ_K, δ_J, and δ_K of this near-prolate rotor could not be determined and they were therefore held fixed at the MP2 values (Table 2) in the weighted least-squares fit. Inclusion of sextic constants did not result in an improved fit and were therefore neglected in the final fit.

The MP2 structure of **I** was employed to calculate the shifts in the rotational constants upon substitution of ^{35}Cl with ^{37}Cl, which were used to predict the spectrum of the $^{37}ClCH_2CH_2PH_2$ species. The ground-state spectrum of this species was found within a few megahertz of the predicted frequencies and seen to be about one-third as intense as the spectrum of the ^{35}Cl species, as expected. A total of 72 ^aR-transitions listed in Table 5S (Supporting Information) were least-squares fitted to obtain the spectroscopic constants shown in Table 3.

The rotational constants of conformers **I** and **II** are calculated (Tables 2 and 2S (Supporting Information)) to be so similar that a definite conformer assignment cannot be made on the basis of the rotational constants alone. The entries in Table 2 indicate that μ_a is the predominant dipole moment component in both these forms. Neither the rotational constants nor the dipole moment components can therefore be used to obtain a safe conformer assignment. Additional evidence is required.

Conformer **I** has C_s symmetry with six out-of-plane hydrogen atoms. A similar situation is found for one of the conformers of $CH_3CH_2PH_2$.[7,8] The value of pseudo inertial defect, $I_c - I_b - I_a$, where I_a, I_b, and I_c are the principal moments of inertia, should therefore be almost constant for the ^{35}Cl and ^{37}Cl species of **I** and have nearly the same value as that of the said $CH_3CH_2PH_2$ conformer. The value of $I_c - I_b - I_a$ is −10.61(1) × 10^{-20} u m^2 for the ^{35}Cl isotopologue, and 10.65(1) for the ^{37}Cl species, as seen from Table 3, almost the same as −10.47 (same units and magnitude), which has been calculated from the rotational constants of $CH_3CH_2PH_2$.[8] Moreover, the substitution coordinates[32] of the chlorine atom calculated from the entries in Table 3 using Kraitchman's equations[33] are $|a| = 216.7(1)$, $|b| = 12.5(3)$, and $|c| = 10.4(3)$ pm, where the uncertainties have been calculated as recommended by van Eijck.[34] The values derived from the MP2 structure are $|a| = 216.0$, $|b| = 5.7$, and $|c| = 0.0$ pm. The agreement is good for $|a|$, and satisfactory for the two small and unreliable $|b|$ and $|c|$ coordinates. Finally, the fact that the theoretical calculations predict that **I** is ~6 kJ/mol more stable than **II** (Tables 2 and 2S (Supporting Information)) is additional evidence indicating that the spectroscopic constants of Table 2 indeed belong to conformer **I**.

Comparison of the theoretical (Table 2) and experimental (Table 3) spectroscopic constants is in order. It is seen from these two tables that the experimental values of each of the rotational constant of the ^{35}Cl species of conformer **I** is about 1% smaller than the MP2 rotational constants. Differences of this order of magnitude have to be expected because the experimental and theoretical rotational constants are defined differently. The experimental constants are effective parameters, whereas the MP2 constants are calculated from an approximate equilibrium structure. The good agreement between theory and experiment seen for the rotational constants is another indication that the MP2 structure shown in Table 1 is accurate, as should be expected.[35] There is also good agreement between the experimental and MP2 centrifugal distortion constants Δ_J and Δ_{JK} (Tables 2 and 3).

Vibrationally Excited States of Conformer I. The MP2 calculations of the harmonic vibrational frequencies (not given in Table 2) predicted that the uncorrected C1−C2 torsional frequency at 112 cm^{-1}, resulting in a Boltzmann factor of 0.58 at room temperature. The uncorrected frequencies and Boltzmann factors were 204 cm^{-1} and 0.37 for the C2−P8 torsion, 208 cm^{-1} and 0.36 for the lowest bending, and 299 cm^{-1} and 0.23 for the second lowest bending vibration. The anharmonic B3LYP values for the same four lowest vibrations were 103, 188, 202, and 286 cm^{-1}, which are not very different from the corresponding harmonic MP2 frequencies. Further frequencies were calculated to be higher than 650 cm^{-1} by both procedures and need not be considered further. The ground-state spectrum should therefore be accompanied by four vibrationally excited-state spectra having about 58, 37, 36, and 23% of the intensity of the ground-vibrational-state spectrum at room temperature,

TABLE 4: Spectroscopic Constants[a] of the First Excited State of the C−C Torsion of the ${}^{35}ClCH_2CH_2PH_2$ and ${}^{37}ClCH_2CH_2PH_2$ Isotopologues of Conformer I

	${}^{35}ClCH_2CH_2PH_2$[b]	${}^{37}ClCH_2CH_2PH_2$[c]
A (MHz)	23554(17)	23544(23)
B (MHz)	1447.0136(33)	1409.8956(35)
C (MHz)	1407.4266(36)	1372.2732(43)
Δ_J (kHz)	0.1499(18)	0.1438(19)
Δ_{JK} (kHz)	−1.33(6)	−1.18(5)
Δ_K (kHz)	57.2[d]	57.2[d]
δ_J (kHz)	0.00538[d]	0.00538[d]
δ_K (kHz)	−0.0148[d]	−0.0148[d]
rms[e]	1.721	1.407
no. of transitions[f]	106	81
$I_c - I_a - I_b$[g] (10^{-20} u m^2)	−11.63(1)	−11.64(2)

[a] *A*-Reduction I^r-representation.[27] Uncertainties represent one standard deviation. [b] The spectrum is listed in Table 4S in the Supporting Information. [c] The spectrum is listed in Table 6S, Supporting Information. [d] Fixed, see text. [e] Root-mean-square deviation of a weighted fit. [f] Number of transitions used in the least-squares fit. [g] Principal moments of inertia. Conversion factor: 505 379.05 MHz 10^{-20} u m^2.

according to these calculations. However, the spectrum deviates significantly from these predictions, as discussed in detail below and seen in Figure 2.

The strongest excited-state band head has an intensity that is about 75% of the intensity of the ground-state band head. An example of this is shown in Figure 2, where the band head of the ground state of the $J = 21 \leftarrow 20$ transition occurs at a frequency of 59 866 MHz, whereas the frequency of the first excited state of the C1−C2 torsion is found at 59 942 MHz. Similar observations were made for all pile-up regions of both chlorine isotopologues.

The assignments of the rotational transitions of the first excited state of the C1−C2 torsion were made in the same fashion as for the ground state. The spectrum of the ${}^{35}Cl$ isotopologue is listed in Table 4S of the Supporting Information, whereas the spectrum of the ${}^{37}Cl$ species is shown in Table 6S (Supporting Information). The spectroscopic constants of this state are displayed in Table 4.

Relative intensity measurement using the band heads of several ground and excited states of this vibration yielded 63(20) cm^{-1} for this torsion, far from the MP2 prediction of 112 cm^{-1}.

It is seen in Tables 3 and 4 that the absolute value of the pseudo inertial defect, $I_c - I_b - I_a$, increases upon excitation, which is typical for an out-of-symmetry-plane vibration.[36] This increase, which is calculated to be 1.02×10^{-20} u m^2 from the entries of Table 3 and 4, can be employed to obtain a rough independent value for the C1−C2 torsion. Following Hanyu et al.,[37] a torsional frequency of 66 cm^{-1} is obtained using this increase in the absolute value, in excellent agreement with the relative intensity measurements above (63(20) cm^{-1}).

Another property of this vibrational mode is evident from the MW spectrum, which can be exemplified with reference to Figure 2. The frequency difference between the two band heads of the first excited state of the torsion and the ground state is 76 MHz. Interestingly, there is no new band head with an intensity of about $0.75 \times 0.75 = 0.56$ of the ground-state band-head intensity at a frequency of approximately 60 018 MHz. A near equidistant progression of frequencies and a smooth progression of intensities are expected for a harmonic vibration. This is clearly not the case for the C1−C2 torsional vibration of rotamer **I**, which is therefore assumed to be strongly anharmonic, or to be in resonance with some other excited-state vibration.

The vibration−rotation constants are defined by $\alpha_X = X_0 - X_1$,[26] where X_0 is the rotational constant of the ground state and X_1 is the corresponding constant of the first excited state of a particular vibrational mode. It is not possible to derive an accurate value for α_A because the A rotational constants of Tables 3 and 4 have large standard deviations. The experimental value of this constant can therefore not be used for a meaningful comparison with the B3LYP predictions. Fortunately, the other two vibration−rotation constants can be employed for this purpose. The experimental value obtained from the rotational constants of Tables 3 and 4 are $\alpha_B = -1.13$ and $\alpha_C = -2.55$ MHz, in excellent agreement with the B3LYP values of −1.19 and −2.35 MHz, respectively (not given in Table 2S, Supporting Information).

It was mentioned above that both the first excited state of the C2−P8 torsion and the first excited state of the lowest bending vibration should produce satellite spectra with roughly 40% of the intensity of the ground state spectrum. No band heads with this relative intensity were observed, which is also evident in Figure 2. However, several band heads with intensities in that are 15−25% of that of the ground-state band-head intensity. The frequencies of some of these band heads are pointed out in Figure 2. Further detailed assignments were not possible for these weak transitions, whose frequencies should be in the ~250−300 cm^{-1} range. It is concluded that the present theoretical calculations are not sufficiently sophisticated to deal satisfactorily with the complicated pattern of vibrationally excited states displayed by rotamer **I**.

Assignment of Conformer II of $ClCH_2CH_2PH_2$. Conformer **II** was predicted to be about ~6 kJ/mol less stable than **I** (Tables 2 and 2S (Supporting Information)). This rotamer too is very prolate ($\kappa \approx -0.996$) and has a statistical weight of 2 relative to **I**, whose statistical weight is presumed to be 1. The occurrence of **II** relative to **I** should be approximately 25%, according to Boltzmann statistics. The fact that this form has a relatively large μ_a indicates that pile-ups separated by the sum of the B and C rotational constants might occur with sufficient intensity to be observable. The sum of B plus C should be about 16.6 MHz larger than $B + C$ of **I** (Table 2). The pile-ups belonging to **II** were therefore expected to occur at higher frequencies than their counterparts belonging to **I**.

A series of pile-ups compatible with these predictions were observed and found to be roughly one-third as intense as the corresponding pile-ups belonging to **I**. A total of 37 ${}^{a}R$-transitions were assigned for the ${}^{35}Cl$ isotopologue and used to determine the spectroscopic constants listed in Table 5. No b- or c-type lines were found. The spectrum is listed in Table 7S in the Supporting Information.

The value of pseudo inertial defect is $-9.997(14) \times 10^{-20}$ u m^2 in this case (Table 5), compared to -9.90×10^{-20} u m^2 calculated from the MP2 rotational constants shown in Table 2, and -9.85×10^{-20} u m^2 calculated for the similar conformer of $CH_3CH_2PH_2$,[7,8] which indicates that the spectrum in Table 7S (Supporting Information) indeed belongs to **II**.

Interestingly, the first excited state of the C1−C2 torsion of this isotopologue appears with an intensity of approximately 75% of the ground-state intensity, just as in the case of conformer **I**. The value of $B + C = 2873.8(2)$ MHz was determined for this excited torsional state. No further excited states of this mode appeared with the expected frequencies and intensities, just as in the case of conformer **I** above. A complicated pattern associated with vibrationally excited states therefore exists for **II** as well.

TABLE 5: Spectroscopic Constants[a,b] of the Ground Vibrational State of the $^{35}ClCH_2CH_2PH_2$ Isotopologue of Conformer II

A (MHz)	24 547(17)
B (MHz)	1456.0328(43)
C (MHz)	1412.9167(54)
Δ_J (kHz)	0.1359(34)
Δ_{JK} (kHz)	−1.21(10)
Δ_K (kHz)	63.3[c]
δ_J (kHz)	0.00640[c]
δ_K (kHz)	0.0656[c]
rms[d]	1.067
no.t[e]	37
$I_c - I_a - I_b$[f] (10^{-20} u m^2)	−9.997(14)

[a] *A*-Reduction I^r-representation.[27] Uncertainties represent one standard deviation. [b] The spectrum is listed in Table 7S, Supporting Information. [c] Fixed, see text. [d] Root-mean-square deviation of a weighted fit. [e] Number of transitions used in the least-squares fit. [f] Principal moments of inertia. Conversion factor: 505 379.05 MHz 10^{-20} u m^2.

It was not possible to obtain a full assignment for the ^{37}Cl form of **II**, because of insufficient intensities. Only the pile-up frequencies could be obtained in this case, yielding $B + C =$ 2796.3(2) MHz. This value is very close to 2795.5 MHz calculated from the changes of the rotational constants of **II** upon ^{37}Cl substitution. This is another indication that the spectrum of **II** has been correctly assigned.

Searches for Further Conformers. The theoretical energy differences between **I** and the other four rotamers (Tables 2 and 2S (Supporting Information)) are not predicted to be excessively large. Searches were therefore made for these conformers among the comparatively weak transitions that had not been assigned, because conformers **III**−**V** are all relatively polar (Table 2 and 2S (Supporting Information)), and they should all have comparatively strong b-type spectra provided they were present in high concentrations. b-type spectra of prolate rotors are generally more difficult to assign than ^{a}R-spectra. Moreover, quadrupole splitting also leads to reduced intensities of the individual b-type transitions to a larger extent than for a-type lines. This and a high energy difference may explain why the searches for the b-type spectra met with no success, but the absence of unassigned strong transitions is taken as evidence that **I** is indeed the preferred form of the title compound, in agreement with the theoretical predictions.

Energy Difference Between II and I. Relative intensity measurements were made on several ^{a}R-band heads of conformers **I** and **II** to determine the energy difference between them, taking into consideration the different dipole moments of the two forms and the complicated nature of the band heads, as well as the statistical weight assumed to be 2 for conformer **II** and 1 for rotamer **I**. It was found that **I** is more stable than **II** by 5.2 kJ/mol. This value has to be assigned a rather large standard deviation, which we conservatively estimate to be 0.6 kJ/mol. The experimental energy difference of 5.2(6) kJ/mol is very close to the MP2 result (5.9 kJ/mol; Table 2) and the B3LYP prediction (6.0 kJ/mol; Table 2S, Supporting Information).

Conclusions

This paper reports the first synthesis of $ClCH_2CH_2PH_2$. This compound is the first halogenated ethylphosphine that has been studied by MW spectroscopy augmented by quantum chemical calculations at the MP2/6-311++(3df,3pd) and B3LYP/6-311++(3df,3pd) levels of theory.

The spectra of two rotameric forms, denoted **I** and **II** and shown in Figure 1, have been assigned. Conformer **I** was found to be 5.2(6) kJ/mol more stable than **II** by relative intensity measurements. The rotational and quartic centrifugal distortion constants calculated from the MP2 structure are in very good agreement with their experimental counterparts. Both computational procedures predict energy differences between **I** and **II** that are close to the experimental energy difference [5.2(6) kJ/mol]. However, this energy difference is quite different from 2.4(12) kJ/mol obtained for the energy difference of the two similar conformers of $CH_3CH_2PH_2$,[7] showing that the introduction of a highly electronegative chlorine atom in the 2-position has a considerable influence on the energy differences.

The first excited states of the C−C torsional vibration of both **I** and **II** were assigned. Its frequency was determined to be 63(20) cm^{-1} for conformer **I** by relative intensity measurements. This vibration has a similar frequency in **II**. It was also found that this normal mode deviates from harmonic behavior. The quantum chemical calculations were found to be unable to predict correct frequencies of this and other low-frequency normal vibrations.

The quantum chemical calculations predict that three further rotamers characterized by a Cl−C−C−P synclinal arrangement, and denoted **III**−**V** in Figure 1, exist at energies that are ~5−12 kJ/mol higher than the energy of **I**. Searches for the MW spectra of these conformers were unsuccessful.

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Supporting Information Available: Results of the B3LYP/6-311++G(3df,3pd) calculations and the microwave spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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