

# Microwave Spectrum, and Conformational Composition of (Chloromethyl)phosphine (ClCH<sub>2</sub>PH<sub>2</sub>)

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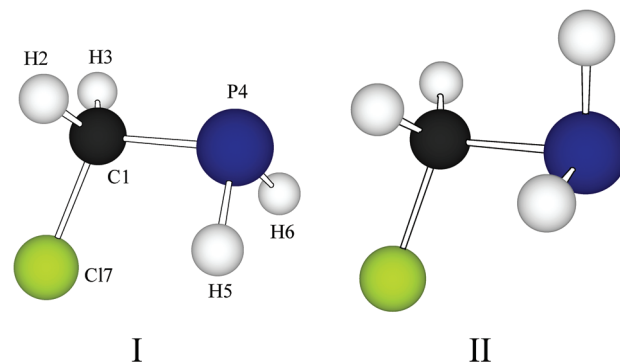
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(Chloromethyl)phosphine, (ClCH<sub>2</sub>PH<sub>2</sub>) has been studied by microwave spectroscopy at  $-30\text{ }^{\circ}\text{C}$  in the 22–80 GHz spectral interval. The experimental study has been augmented by quantum chemical calculations at the MP2/aug-cc-pVQZ and B3LYP/aug-cc-pVTZ levels of theory. The spectra of the ground as well as of several vibrationally excited states of the <sup>35</sup>ClCH<sub>2</sub>PH<sub>2</sub> and <sup>37</sup>ClCH<sub>2</sub>PH<sub>2</sub> isotopologues of two rotameric forms, denoted **I** and **II**, have been assigned. These conformers have different orientations of the phosphino group. **I** has a symmetry plane, consisting of the Cl–C–P link of atoms, whereas the phosphino group is rotated out of this symmetry plane in **II**. Conformer **I** was found to be 4.3(5) kJ/mol more stable than **II** by relative intensity measurements. The rotational and quartic centrifugal distortion constants calculated using the MP2/aug-cc-pVQZ procedure are in very good agreement with their experimental counterparts. Less good agreement is found in the B3LYP/aug-cc-pVTZ calculations. Both computational procedures predict energy differences between **I** and **II** that are close to the experimental energy difference. It is suggested that **I** is the preferred form of this molecule because it is stabilized by weak intramolecular hydrogen bonding between the chlorine atom and the hydrogen atoms of the phosphino group. Repulsion between the lone electron pair of the phosphorus atom and the chlorine atom also stabilizes **I** relative to **II**.

## Introduction

Microwave (MW) spectroscopy has over the years been employed to investigate several phosphines such as CH<sub>3</sub>PH<sub>2</sub>,<sup>1</sup> (CH<sub>3</sub>)<sub>2</sub>PH,<sup>2,3</sup> (CH<sub>3</sub>)<sub>3</sub>CPH<sub>2</sub>,<sup>4</sup> (CH<sub>3</sub>)<sub>3</sub>P,<sup>5</sup> (CH<sub>3</sub>)<sub>2</sub>CHPH<sub>2</sub>,<sup>6</sup> CH<sub>3</sub>CH<sub>2</sub>PH<sub>2</sub>,<sup>7,8</sup> cyclopropylphosphine (C<sub>3</sub>H<sub>5</sub>PH<sub>2</sub>),<sup>9</sup> H<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>C≡N,<sup>10</sup> HC≡CPH<sub>2</sub>,<sup>11</sup> H<sub>2</sub>C=CHPH<sub>2</sub>,<sup>12,13</sup> H<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>,<sup>14</sup> HC≡CCH<sub>2</sub>PH<sub>2</sub>,<sup>15</sup> H<sub>2</sub>C=CHCH<sub>2</sub>PH<sub>2</sub>,<sup>16</sup> H<sub>2</sub>C=C=CHPH<sub>2</sub>,<sup>17</sup> phosphirane (C<sub>2</sub>H<sub>5</sub>P),<sup>18</sup> (cyclopropylmethyl)phosphine (C<sub>3</sub>H<sub>5</sub>CH<sub>2</sub>PH<sub>2</sub>),<sup>19</sup> cyclopentadienylphosphine (C<sub>5</sub>H<sub>5</sub>PH<sub>2</sub>),<sup>20</sup> and (2-chloroethyl)phosphine, ClCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>.<sup>21</sup> Most of these compounds have only one rotameric form, but two or more conformers have been demonstrated to exist for each of CH<sub>3</sub>CH<sub>2</sub>PH<sub>2</sub>,<sup>7,8</sup> H<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>C≡N,<sup>10</sup> H<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>,<sup>14</sup> H<sub>2</sub>C=CHCH<sub>2</sub>PH<sub>2</sub>,<sup>16</sup> H<sub>2</sub>C=C=CHPH<sub>2</sub>,<sup>22</sup> C<sub>3</sub>H<sub>5</sub>CH<sub>2</sub>PH<sub>2</sub>,<sup>19</sup> and C<sub>5</sub>H<sub>5</sub>PH<sub>2</sub>.<sup>20</sup> Moreover, a series of phosphines, including the title compound, (chloromethyl)phosphine (ClCH<sub>2</sub>PH<sub>2</sub>), has recently been investigated by gas electron diffraction and quantum chemical calculations and their conformational and structural properties have been compared to the corresponding amines.<sup>23</sup> It was concluded in this study that the conformational and structural properties of phosphines are often different from their amine analogues.<sup>23</sup>

In this work, the microwave studies of phosphines are extended to include ClCH<sub>2</sub>PH<sub>2</sub>. The conformational properties of this compound must be largely determined by the interaction between the chlorine atom and the phosphino group. Very few studies have dealt with this kind of interaction in the past. However, one example is the very recent study of (2-chloro-



**Figure 1.** Model of ClCH<sub>2</sub>PH<sub>2</sub> with atom numbering. The MW spectra of conformers **I** and **II** were assigned. **I** was found to be 4.3(5) kJ/mol more stable than **II** by relative intensity measurements. MP2 and B3LYP calculations predict **I** to be favored by ~4 kJ/mol relative to **II**.

ethyl)phosphine, ClCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>,<sup>21</sup> where no Cl–C–C–P synclinal conformers were found by MW spectroscopy, which indicates that there is no significant attraction between the chlorine atom and the phosphino group. The chlorine atom and the phosphino group are brought into much closer proximity in the title compound than in the synclinal forms of (2-chloroethyl)phosphine. This may influence the conformational properties of ClCH<sub>2</sub>PH<sub>2</sub> to a larger extent than what is the case in its congener ClCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>.

Electron-diffraction and quantum-chemical calculations<sup>23,24</sup> have shown that there are two conformers, which are depicted in Figure 1 and denoted **I** and **II**, respectively. **I** has a symmetry plane (*C<sub>s</sub>* symmetry) and the H–P–C–Cl dihedral angles are (+) or (–) synclinal, roughly +60°, or –60° from synperiplanar (0°), whereas **II** has no symmetry plane. One of the H–P–C–Cl

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dihedral angles is synclinal, while the other is antiperiplanar (about  $180^\circ$  from synperiplanar). It was found in these studies that **I** is the preferred form by about 4 kJ/mol.<sup>23,24</sup>

A successful investigation of a delicate conformational equilibrium such as the one presented by (chloromethyl)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.** (Chloromethyl)phosphine is malodorous, pyrophoric, and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.

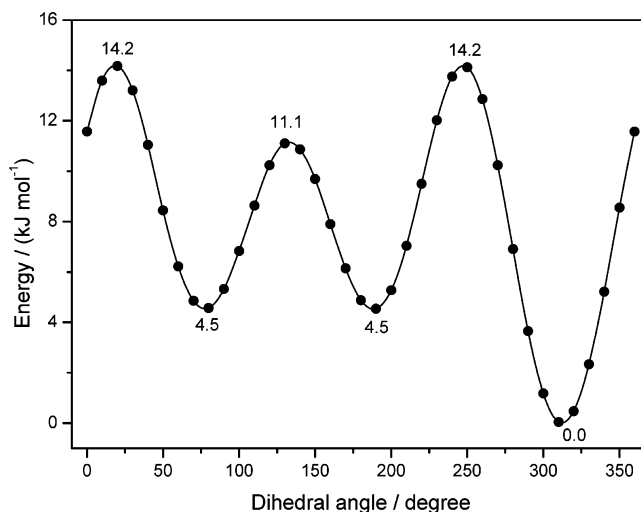
**Synthesis.** (Chloromethyl)phosphine has been prepared as previously reported,<sup>25</sup> but we started from 2-(chloromethyl)-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane<sup>26</sup> in the present case. This phosphonate was used instead of (chloromethyl)phosphonic acid diethyl ester to avoid the presence of small amounts of ethanol in the product.<sup>27</sup>

**Microwave Experiment.** The spectrum of (chloromethyl)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.<sup>20,28</sup> This spectrometer has a resolution of about 0.5 MHz and measures the frequency of isolated transitions with an estimated accuracy of  $\approx 0.10$  MHz. The experiments were performed at about  $-30^\circ\text{C}$  by cooling the 2 m Hewlett-Packard absorption cell with portions of dry ice. The pressure of  $\text{ClCH}_2\text{PH}_2$  was roughly 10 Pa during the measurements.

**Quantum Chemical Methods.** The present ab initio and density functional theory (DFT) calculations were performed by employing the Gaussian 03 suite of programs,<sup>29</sup> 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).<sup>30</sup> Becke's three-parameter hybrid functional<sup>31</sup> employing the Lee, Yang, and Parr correlation functional (B3LYP)<sup>32</sup> was employed in the density functional theory (DFT) calculations. Peterson and Dunning's<sup>33</sup> correlation-consistent triple- and quadruple- $\zeta$  wave function augmented with diffuse functions, aug-cc-pVTZ and aug-cc-pVQZ, were used in the calculations. Calculations of nuclear quadrupole coupling constants of the chlorine nucleus in the principal-inertial axis system were performed using Bailey's program,<sup>34</sup> which employs the electric field gradient obtained in the Gaussian 03 calculations. The present quantum chemical calculations are at a higher level of theory than those previously reported.<sup>23,24</sup>

## Results and Discussion

**Quantum-Chemical Calculations.** The potential curve for rotation about the C1–P4 bond was first calculated at the B3LYP/aug-cc-pVTZ level by varying the C17–C1–P4–H5 dihedral angle a total of  $360^\circ$ , in steps of  $10^\circ$ . The resulting curve (Figure 2) was found to have three minima and two maxima. Two of the minima have identical energies corresponding to the two mirror-image forms of **II**. The energies, structures, dipole moments, vibrational frequencies, Watson's quartic, and sextic centrifugal distortion constants<sup>35</sup> and



**Figure 2.** B3LYP/6-311++G(3df,3pd) potential curve for the rotation about the C1–P4 bond. The values of the H5–P4–C1–C17 dihedral angle are given on the abscissa, whereas the energies in kJ/mol are given on the ordinate. Conformer **I** has the lowest energy indicated on the figure by 0 kJ/mol for a value of the H5–P4–C1–C17 dihedral angle of  $312.3^\circ$  ( $-47.7^\circ$ ). Rotamer **II** is higher in energy by 4.5 kJ/mol relative to **I**. There are two mirror-image forms of **II** that have the same energy. The corresponding H5–P4–C1–C17 dihedral angle is  $77.5^\circ$  in one of these, and  $171.6^\circ$  in the other. The maxima have higher energies than **I** by 14.2 and 11.1 kJ/mol, respectively. The corresponding dihedral angles are  $18.5^\circ$ ,  $133.1^\circ$ , and  $247.5^\circ$ , respectively. The lowest torsional level of conformer **I** occurs at 1.39 kJ/mol ( $110\text{ cm}^{-1}$ ) above the bottom of the well at  $312.3^\circ$ . The corresponding energy level of **II** appears at 1.02 kJ/mol ( $85\text{ cm}^{-1}$ ) above the minima at  $77.5^\circ$  and  $171.6^\circ$ .

vibration–rotation constants (the  $\alpha$ 's<sup>36</sup>) were calculated for **I** and **II**. Calculation of vibration–rotation constants is very costly and only B3LYP calculations were performed for these parameters. No imaginary vibrational frequencies were found for each of **I** and **II**, which indicates that they are indeed minima on the conformational-energy hypersurface. Conformer **I** was calculated to be the global-energy minimum, with an electronic energy that is 4.5 kJ/mol lower than that of **II**. This conformer has a symmetry plane. The maxima of the potential curve were located using the transition-state option of Gaussian 03. Their energies were calculated to be 11.1 and 14.2 kJ/mol higher than the energy of **I**. One imaginary vibrational frequency associated with the torsion about the C1–P4 bond was found in each case, which demonstrates that they are first-order transition states.

It is known that MP2 structures are close to equilibrium structures provided a large basis set has been employed.<sup>37</sup> The energies, structures, rotational constants, quartic centrifugal distortion constants, and dipole moments were calculated for conformers **I** and **II** at the MP2/aug-cc-pVQZ level. The geometry optimizations were performed by observing the default convergence criteria of Gaussian 03.<sup>23</sup> No imaginary vibrational frequencies were found for **I** and **II** in these calculations.

The MP2/aug-cc-pVQZ and B3LYP/aug-cc-pVTZ structures are shown in Table 1, together with relevant structural parameters obtained in the electron-diffraction work. The rotational constants calculated from the MP2 and B3LYP structures are shown in Table 2, together with Watson's *S*-reduction quartic centrifugal distortion constants,<sup>35</sup> 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 in this table have been corrected for zero-point vibrational energies. The MP2 harmonic vibrational frequencies of the fundamental

**TABLE 1: MP2,<sup>a</sup> B3LYP,<sup>b</sup> and GED Geometries of Conformers I and II of ClCH<sub>2</sub>PH<sub>2</sub>**

	I			II		
	MP2	B3LYP	GED <sup>c</sup>	MP2	B3LYP	GED <sup>c</sup>
Bond Length (pm)						
C1–H2	108.6	108.6		108.4	108.4	
C1–H3	108.6	108.6		108.6	108.6	
C1–P4	184.5	185.9	186.8	185.6	187.3	187.9
C1–Cl7	178.1	181.4		178.0	180.8	
P4–H5	140.9	141.8	142.7	141.4	142.5	142.7
P4–H6	140.9	141.8		141.0	142.0	
Angle (deg)						
H2–C1–H3	108.3	108.6		109.6	109.6	
H2–C1–H4	109.0	109.0		113.6	113.7	
H2–C1–Cl7	107.4	106.5		107.4	106.8	
H3–C1–P4	109.0	109.0		109.6	109.4	
H3–C1–Cl7	107.4	106.5		107.5	106.9	
P4–C1–Cl7	115.7	117.0		108.8	110.1	
C1–P4–H5	96.6	97.5	97.0	95.5	95.1	97.0
C1–P4–H6	96.6	97.5		96.0	96.6	
H5–P4–H6	94.3	94.4	94.7	93.8	93.5	94.7
Dihedral Angle (deg)						
H2–C1–P4–H5	73.4	73.1		–49.3	–51.8	
H2–C1–P4–H6	168.6	168.5		45.1	42.3	
H3–C1–P4–H5	–168.6	–168.5		73.7	71.2	
H3–C1–P4–H6	–73.4	–73.1		168.2	165.3	
Cl7–C1–P4–H5	–47.6	–47.7		–169.0	–171.6	
Cl7–C1–P4–H6	47.6	47.7		–74.5	–77.5	

<sup>a</sup> Basis set: aug-cc-pVQZ. Total energy for **I**: –2208 187.4 kJ/mol. Total energy for **II**: –2208 183.2 kJ/mol. <sup>b</sup> Basis set: aug-cc-pVTZ. Total energy for **I**: –2211 042.0 kJ/mol. Total energy for **II**: –2211 037.4 kJ/mol. <sup>c</sup> From electron-diffraction works.<sup>23,24</sup>

**TABLE 2: Parameters of Spectroscopic Interest of the Two Conformers of ClCH<sub>2</sub>PH<sub>2</sub>**

	I		II	
	MP2 <sup>a</sup>	B3LYP <sup>b</sup>	MP2 <sup>a</sup>	B3LYP <sup>b</sup>
Rotational Constants (MHz)				
A	25852.4	25905.1	24817.9	24867.4
B	3125.2	3004.3	3255.4	3131.0
C	2907.3	2804.1	2993.6	2890.2
Pseudo Inertial Defect <sup>c</sup> (10 <sup>–20</sup> u m <sup>2</sup> )				
Δ	–7.38	–7.50	–6.78	–6.87
Quartic Centrifugal Distortion Constants <sup>d</sup> (kHz)				
D <sub>J</sub>	1.34	1.31	1.83	1.72
D <sub>JK</sub>	–19.0	–19.0	–27.2	–25.5
D <sub>K</sub>	248.5	271.4	268.8	282.7
d <sub>1</sub>	–0.164	–0.152	–0.262	–0.234
d <sub>2</sub>	–0.00347	–0.00300	–0.00622	–0.00529
Dipole Moment <sup>e</sup> (10 <sup>–30</sup> C m)				
μ <sub>a</sub>	2.73	3.02	4.23	4.06
μ <sub>b</sub>	2.41	2.30	5.66	5.22
μ <sub>c</sub>	0.00 <sup>f</sup>	0.00 <sup>f</sup>	2.21	1.88
Energy Difference <sup>g</sup> (kJ/mol)				
ΔE	0.0	4.0	0.0	4.2

<sup>a</sup> Basis set: aug-cc-pVQZ. <sup>b</sup> Basis set: aug-cc-pVTZ. <sup>c</sup> Defined by  $\Delta = I_a - I_b - I_c$ , where  $I_a$ ,  $I_b$ , and  $I_c$  are the principal axes moments of inertia. Conversion factor: 505 379.05 × 10<sup>–20</sup> MHz u m<sup>2</sup>. <sup>d</sup> S-reduction.<sup>35</sup> <sup>e</sup> 1 Debye = 3.33654 × 10<sup>–30</sup> C m. <sup>f</sup> For symmetry reasons. <sup>g</sup> Relative to the energy of conformer **I** and corrected for zero-point vibrational energy.

vibrations of **I** are listed in Table 1S, while the frequencies of **II** are found in Table 2S in the Supporting Information. The B3LYP harmonic and anharmonic vibrational frequencies of **I**

and **II** are listed in Tables 3S and 5S, respectively, while the vibration–rotation constants<sup>36</sup> are listed in the Tables 4S and 6S.

There are some noteworthy differences in the MP2 and B3LYP structures particularly associated with the C1–Cl7 and C1–P4 bonds. The B3LYP C1–Cl7 bond lengths are roughly 3 pm longer than the corresponding MP2 bond lengths (Table 1). The C–Cl equilibrium ( $r_e$ ) bond length in CH<sub>3</sub>Cl has been determined to be 177.5(2) pm.<sup>38</sup> This value is therefore much closer to the MP2 predictions (Table 1) for **I** (178.1 pm) and for **II** (178.0 pm), than to the B3LYP results.

The MP2 C1–P4 bond lengths are 184.5 in **I** and 185.6 pm in **II** (Table 1). Both these bond lengths are predicted to be about 1.5 pm shorter than their B3LYP counterparts. The  $r_g$ -value for the corresponding bond length in CH<sub>3</sub>PH<sub>2</sub> is 185.8(3) pm.<sup>39</sup> Equilibrium bond lengths are available for a similar phosphine, namely CH<sub>3</sub>CH<sub>2</sub>PH<sub>2</sub>.<sup>40</sup> A  $r_e$  value of 185.29(1) pm for this bond length has been reported<sup>40</sup> for one of the conformers ethylphosphine, whereas  $r_e$  = 184.91(3) pm was found for a second rotamer of this compound.<sup>40</sup> These values are closer to the MP2 predictions (184.5 and 185.6 pm; Table 1) than to the B3LYP results (185.9 and 187.3 pm; Table 1). However, the present comparisons of compounds that only contain the chlorine atom or the phosphino group do not take into account the fact that the C–Cl and C–P bond lengths may be coupled in ClCH<sub>2</sub>PH<sub>2</sub>, which means that these comparisons should be regarded with some caution. It is also noted that 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 result of all this is that the corresponding MP2 and B3LYP rotational constants calculated from the structures in Table 1 are rather similar, whereas differences of 3–4% are seen for *B* and *C* (Table 2).

The quartic centrifugal distortion constants (Table 2) predicted by the two methods vary by up to about 10% and the B3LYP dipole moments tend to be lower than their MP2 counterparts, which is typical. Both MP2 and B3LYP predict an energy difference of about 4 kJ/mol between the two forms with **I** as the more stable rotamer.

The quadrupole coupling constants were calculated using the MP2 structure. The values of these constants were predicted to be  $\chi_{aa} = -37.94$ ,  $\chi_{bb} = 3.14$ , and  $|\chi_{ab}| = 48.48$  MHz for <sup>35</sup>Cl species, and  $\chi_{aa} = -30.17$ ,  $\chi_{bb} = 2.75$  MHz, and  $|\chi_{ab}| = 38.09$  MHz for the <sup>37</sup>Cl isotopologue of conformer **I**, while  $\chi_{aa} = -34.32$ ,  $\chi_{bb} = -1.94$  MHz, and  $|\chi_{ab}| = 49.20$  MHz were predicted for the <sup>35</sup>Cl variant, and  $\chi_{aa} = -27.04$ ,  $\chi_{bb} = -1.53$ , and  $|\chi_{ab}| = 38.68$  MHz for the <sup>37</sup>Cl species of **II**. Bailey's procedure<sup>34</sup> were used in these calculations.

**Microwave Spectrum and Assignment of the Spectrum of Conformer I of ClCH<sub>2</sub>PH<sub>2</sub>** This rotamer is predicted to be the preferred form of the molecule by ~4 kJ/mol relative to **II** in both the MP2 and the B3LYP calculations (Table 2). There are two naturally occurring isotopes of chlorine, namely, <sup>35</sup>Cl (75.5%) and <sup>37</sup>Cl (24.5%). Both isotopologues of **I** are nearly prolate rotors (Ray's asymmetry parameter<sup>41</sup>  $\kappa \sim -0.98$  in each case).  $\mu_a$ , which is the largest dipole moment component of **I**, is roughly 3 × 10<sup>–30</sup> C m (Table 2). Pile-ups of <sup>a</sup>R-branch transitions separated by approximately  $B + C \sim 6.0$  GHz (Table 2) for the <sup>35</sup>Cl isotopologue were therefore expected to occur for this form and to be a prominent feature of the spectrum. Comparatively strong b-type transitions were also expected to be present because the size of  $\mu_b$  (2.5 × 10<sup>–30</sup> C m; Table 2) should be similar to that of  $\mu_a$ . The b-type spectrum should be



much richer than the a-type spectrum and consist of a large number of P-, Q-, and R-branch transitions.

Survey spectra revealed a dense and complex spectrum with absorption lines occurring every few megahertz throughout the entire spectrum, as expected. The series of the comparatively strong <sup>a</sup>R-branch pile-ups protruded from the background of weaker lines and were found close to their predicted frequencies. Detailed assignments of the a-type R-branch transitions of both the <sup>35</sup>Cl and <sup>37</sup>Cl species were readily made. No splittings caused by quadrupole coupling of the chlorine nuclei with the overall rotation were observed for these lines, which, however, appeared to be relatively broad. Calculations using the theoretical nuclear quadrupole coupling constants of the previous section were used to calculate splittings caused by this effect employing program MB09.<sup>42</sup> It was found that the strongest components of this <sup>a</sup>R-type hyperfine structure were split by less than the resolution of the spectrometer (about 0.5 MHz).

The preliminary spectroscopic constants obtained from the a-type lines were then used to predict the spectral positions of b-type transitions. Calculations by MB09 of the quadrupole interaction indicated that many of the b-type lines involving low values of the pseudo quantum number  $K_{-1}$  should display much larger splittings than found for the a-type transitions, whereas lines involving  $K_{-1} > 2$  would not be split sufficiently to be resolved. Assignments of b-type lines were first made for the comparatively strong Q-branch  $K_{-1} = 1 \leftarrow 0$  lines. The observed splittings, whose sizes could be well predicted using the theoretical quadrupole coupling constants above, were useful for making the first assignments, which were gradually extended to include b-type P-, Q-, and R-branch transitions of higher and higher values of the  $J$  and  $K_{-1}$  quantum numbers, up to  $J = 86$  and  $K_{-1} = 13$  for the <sup>35</sup>Cl species and  $J = 58$  and  $K_{-1} = 9$  for the <sup>37</sup>Cl species. Transitions involving even higher values of the quantum numbers were searched for but not found presumably because of an unfavorable Boltzmann factor making them not very intense. The weighted least-squares fits were performed employing Watson's  $S$ -reduction Hamiltonian with the  $I$ -representation,<sup>35</sup> using Sørensen's program Rotfit.<sup>43</sup> Attempts were made to determine accurate experimental values of the nuclear quadrupole constants  $\chi_{aa}$  and  $\chi_{bb}$ , but least-squares fitting of the observed quadrupole splitting resulted in rather inaccurate values for these constants. It was therefore decided to use the theoretical values of  $\chi_{aa}$  and  $\chi_{bb}$  of the previous section to make corrections for this effect, when necessary. A total of 288 transitions, which are listed in Table 7S in the Supporting Information and corrected for quadrupole interactions, were used to obtain the spectroscopic constants of <sup>35</sup>ClCH<sub>2</sub>PH<sub>2</sub> shown in Table 3. Similarly, 141 transitions (see Table 10S) yielded the spectroscopic constants of <sup>37</sup>ClCH<sub>2</sub>PH<sub>2</sub> displayed in the same table.

Conformer **I** has  $C_s$  symmetry with four out-of-plane hydrogen atoms, two from the ClCH<sub>2</sub> moiety, and two from the phosphino group. The value of the pseudo inertial defect,  $\Delta = I_c - I_b - I_a$ , where  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia, should therefore be almost constant for the <sup>35</sup>Cl and <sup>37</sup>Cl species. The value of  $\Delta$  is  $-7.379837(50) \times 10^{-20} \text{ u m}^2$  for the <sup>35</sup>Cl isotopologue, and  $-7.37847(20) \times 10^{-20} \text{ u m}^2$  for the <sup>37</sup>Cl species, as seen from Table 3. These values are almost the same as  $-7.38$  (same units and magnitude), obtained in the MP2 calculations shown in Table 2. Moreover, the substitution coordinates<sup>44</sup> of the chlorine atom calculated from the entries in Table 3 using Kraitchman's equations<sup>45</sup> are  $|a| = 148.6(2)$  and  $|b| = 18.1(17) \text{ pm}$ , while a small imaginary value was found for the  $c$ -coordinate, which is actually zero for symmetry

**TABLE 3: Spectroscopic Constants<sup>a</sup> of the Ground Vibrational State of Conformer I of ClCH<sub>2</sub>PH<sub>2</sub>**

species	<sup>35</sup> ClCH <sub>2</sub> PH <sub>2</sub> <sup>b</sup>	<sup>37</sup> ClCH <sub>2</sub> PH <sub>2</sub> <sup>c</sup>
$A/\text{MHz}$	25682.2560(93)	25602.110(13)
$B/\text{MHz}$	3097.2779(13)	3017.6089(20)
$B/\text{MHz}$	2880.1929(13)	2810.1917(27)
$D_J/\text{kHz}$	1.3617(66)	1.2522(28)
$D_{JK}/\text{kHz}$	-18.939(30)	-19.268(35)
$D_K/\text{kHz}$	255.39(21)	258.54(37)
$d_1/\text{kHz}$	-0.16255(37)	-0.1651(26)
$d_2/\text{kHz}$	-0.00347(15)	0.0007(10)
$\Phi_J/\text{Hz}$	0.00744(66)	$d$
$\Phi_{JK}/\text{Hz}$	0.247(28)	$d$
$\Phi_{KJ}/\text{Hz}$	-2.41(29)	$d$
$\Phi_K/\text{Hz}$	21.2(37)	$d$
$\Delta/10^{-20} \text{ u m}^2$	-7.379837(50)	-7.37847(20)
rms <sup>g</sup>	1.372	1.723
no. of trans <sup>h</sup>	288	141

<sup>a</sup>  $S$ -reduction  $I$ -representation.<sup>35</sup> Uncertainties represent one standard deviation. <sup>b</sup> Spectrum in Table 7S in the Supporting Information. <sup>c</sup> Spectrum in Table 10S in the Supporting Information. <sup>d</sup> Preset at zero. <sup>e</sup> Further sextic constants preset at zero. <sup>f</sup> Pseudo inertial defect defined by  $I_c - I_a - I_b$ , where  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia. Conversion factor:  $505.379.05 \times 10^{-20} \text{ MHz u m}^2$ . <sup>g</sup> Weighted root-mean-square deviation. <sup>h</sup> Number of transitions used in the fit.

reasons. The uncertainties have been calculated as recommended by van Eijck.<sup>46</sup> The values derived from the MP2 structure are  $|a| = 148.0$ ,  $|b| = 18.0$ , and  $|c| = 0.0 \text{ pm}$  in excellent agreement with the substitution coordinates.

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 rotational constant of the <sup>35</sup>Cl species of conformer **I** is about 0.3–0.8% smaller than the MP2 rotational constants, while the B3LYP rotational constants deviate somewhat more (up to roughly 3%), which is another indication that the MP2 structure is more accurate than the B3LYP structure. It has been pointed out that MP2 structures obtained using a large basis set are generally close to the equilibrium structures,<sup>37</sup> which seems to be the case in the present example as well. There is also very good agreement between the experimental and MP2 quartic centrifugal distortion constants (Tables 2 and 3).

#### Spectra of Vibrationally Excited States of Conformer I.

The MP2 and B3LYP calculations of the harmonic vibrational frequencies (Table 1S, Supporting Information) indicate that there are two fundamental frequencies below about  $600 \text{ cm}^{-1}$ . The lowest of these frequencies is the torsion about the C1–P4 bond, whose uncorrected MP2 value is  $232 \text{ cm}^{-1}$ , whereas the lowest bending vibration is  $252 \text{ cm}^{-1}$  according to these calculations. The B3LYP results were similar (Table 3S, Supporting Information). The ground-state spectrum should therefore be accompanied by two fairly intense spectra originating from the first excited state of the torsion and lowest bending vibration, respectively.

The B3LYP rotation–vibration constants given in Table 4S in the Supporting Information were subtracted from the rotational constants of the ground vibrational state (Table 3) to get a first estimate of the rotational constants of the two lowest excited states. The spectra were subsequently assigned in the same manner as described above for the ground vibrational state. The final fits of the <sup>35</sup>Cl variant are listed in Tables 8S and 9S of the Supporting Information, while their <sup>37</sup>Cl counterparts are displayed in Tables 11S and 12S. Only <sup>a</sup>R-branch lines were assigned for <sup>37</sup>ClCH<sub>2</sub>PH<sub>2</sub> resulting in rather large standard

**TABLE 4: Spectroscopic Constants<sup>a</sup> of Vibrationally Excited States of Conformer I of ClCH<sub>2</sub>PH<sub>2</sub>**

	<sup>35</sup> ClCH <sub>2</sub> PH <sub>2</sub>		<sup>37</sup> ClCH <sub>2</sub> PH <sub>2</sub>	
	lowest torsion <sup>b</sup>	lowest bending <sup>c</sup>	lowest torsion <sup>d</sup>	lowest bending <sup>e</sup>
<i>A</i> /MHz	25949.30(12)	25559.762(93)	25807(11)	25462.5(79)
<i>B</i> /MHz	3095.7605(69)	3090.2216(61)	3016.265(12)	3010.722(14)
<i>B</i> /MHz	2875.9843(69)	2875.6672(63)	2806.165(18)	2805.791(18)
<i>D<sub>J</sub></i> /kHz	1.333(23)	1.392(22)	1.266(28)	1.255(33)
<i>D<sub>JK</sub></i> /kHz	−21.08(29)	−17.23(20)	−21.03(33)	−16.09
<i>D<sub>K</sub></i> /kHz	255.39 <sup>f</sup>	255.39 <sup>f</sup>	258.54 <sup>f</sup>	258.54 <sup>f</sup>
<i>d<sub>1</sub></i> /kHz	−0.1807(58)	−0.1582(33)	−0.1651 <sup>f</sup>	−0.1651 <sup>f</sup>
<i>d<sub>2</sub></i> /kHz	−0.0059(15)	0.00299(83)	0.00067 <sup>f</sup>	0.00067 <sup>f</sup>
$\Delta^g/10^{-20}$ u m <sup>2</sup>	−7.00054(34)	−7.57058(30)	−7.0384(82)	−7.5878(66)
rms <sup>h</sup>	1.645	1.813	1.153	1.624
no. of trans <sup>i</sup>	56	66	23	28

<sup>a</sup> *S*-reduction *F*-representation.<sup>35</sup> Uncertainties represent one standard deviation. <sup>b</sup> Spectrum in Table 8S in the Supporting Information. <sup>c</sup> Spectrum in Table 9S in the Supporting Information. <sup>d</sup> Spectrum in Table 11S in the Supporting Information. <sup>e</sup> Spectrum in Table 12S in the Supporting Information. <sup>f</sup> Fixed. <sup>g</sup> Pseudo-inertial defect defined by  $\Delta = I_c - I_a - I_b$ , where  $I_a$ ,  $I_b$ , and  $I_c$ , are the principal moments of inertia. Conversion factor:  $505\,379.05 \times 10^{-20}$  MHz u m<sup>2</sup>. <sup>h</sup> Weighted root-mean-square deviation. <sup>i</sup> Number of transitions used in the fit.

deviations for the *A* rotational constant. The spectroscopic constants of these excited states are listed in Table 4.

It is seen from this table and Table 3 that the absolute value of the pseudo inertial defect,  $\Delta$ , decreases for the first excited state of the phosphino-group torsion, whereas an increase is seen for the lowest bending vibration. This is in accord with expectations.<sup>47,48</sup>

Relative intensity measurement performed on <sup>3</sup>R-branch transitions observing most of the precautions of Esbitt and Wilson, yielded 229(30) cm<sup>−1</sup> for the torsion and 217(30) cm<sup>−1</sup> for the lowest bending vibration, in satisfactory agreement with the calculated frequencies (Tables 1S and 3S, Supporting Information).

The vibration–rotation constants calculated from the entries in Tables 3 and 4 assuming that  $\alpha_X = X_0 - X_1$ ,<sup>36</sup> 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, yielded  $\alpha_A = -267.04$ ,  $\alpha_B = 7.08$ , and  $\alpha_C = 4.21$  MHz for the torsion about the C1–P4 bond of the <sup>35</sup>Cl species compared to the B3LYP values of  $\alpha_A = -288.51$ ,  $\alpha_B = 0.04$ , and  $\alpha_C = 3.30$  MHz (Table 4S, Supporting Information). Similarly, the experimental vibration–rotation constants of the lowest bending vibration are  $\alpha_A = 122.50$ ,  $\alpha_B = 7.06$ , and  $\alpha_C = 4.52$  MHz, respectively, compared to the theoretical  $\alpha_A = 209.59$ ,  $\alpha_B = 2.70$ , and  $\alpha_C = 1.49$  MHz (Table 4S, Supporting Information). The agreement between the experimental and theoretical vibration–rotation constants of these two states is not perfect, but the signs and the order of magnitude of the calculated constants are correct.

**Assignment of the Spectrum of Conformer II of ClCH<sub>2</sub>PH<sub>2</sub>.** Conformer II was predicted to be about ~4 kJ/mol less stable than I (Table 2). This rotamer has a statistical weight of 2 relative to I, whose statistical weight is presumed to be 1. The concentration of II relative to I should be roughly 25%, according to Boltzmann statistics. This conformer is also very prolate ( $\kappa \approx -0.98$ ) and has nonzero dipole moment components along all three principal inertial axes (Table 2), with  $\mu_b$  as its largest component ( $\sim 5.5 \times 10^{-30}$  C m). The fact that this form has a relatively large  $\mu_a$  of  $\sim 4 \times 10^{-30}$  C m (Table 2) indicates that pile-ups, separated approximately by the sum of the *B* and *C* rotational constants, might be a good starting point in the assignment procedure.

A series of <sup>3</sup>R-pile-ups compatible with these predictions were indeed observed and found to be roughly 1/3 as intense as the corresponding pile-ups belonging to I. b-type lines were added

**TABLE 5: Spectroscopic Constants<sup>a</sup> of the Ground Vibrational State of Conformer II of ClCH<sub>2</sub>PH<sub>2</sub>**

	<sup>35</sup> ClCH <sub>2</sub> PH <sub>2</sub> <sup>b</sup>	<sup>37</sup> ClCH <sub>2</sub> PH <sub>2</sub> <sup>c</sup>
<i>A</i> /MHz	24658.17(14)	24578.78(28)
<i>B</i> /MHz	3225.8737(44)	3143.2741(74)
<i>C</i> /MHz	2965.8516(42)	2894.7721(69)
<i>D<sub>J</sub></i> /kHz	1.810(17)	1.689(25)
<i>D<sub>JK</sub></i> /kHz	−24.97(21)	−24.55(54)
<i>D<sub>K</sub></i> /kHz	298(29)	271(75)
<i>d<sub>1</sub></i> /kHz	−0.25041(98)	−0.2406(23)
<i>d<sub>2</sub></i> /kHz	−0.00630(40)	−0.00472(73)
$\Delta^d/10^{-20}$ u m <sup>2</sup>	−6.76033(14)	−6.75933(21)
rms <sup>e</sup>	1.410	1.634
no. of trans <sup>f</sup>	85	58

<sup>a</sup> *S*-reduction *F*-representation.<sup>35</sup> Uncertainties represent one standard deviation. <sup>b</sup> Spectrum in Table 13S in the Supporting Information. <sup>c</sup> Spectrum in Table 15S in the Supporting Information. <sup>d</sup> Pseudo inertial defect defined by  $I_c - I_a - I_b$ , where  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia. Conversion factor:  $505\,379.05 \times 10^{-20}$  MHz u m<sup>2</sup>. <sup>e</sup> Weighted root-mean-square deviation. <sup>f</sup> Number of transitions used in the fit.

next to the least-squares fit in a manner similar to that described above for I using the calculated quadrupole coupling constants (see above) to correct for this interaction. A total of 85 a- and b-type transitions were assigned for the <sup>35</sup>Cl isotopologue and used to determine the spectroscopic constants displayed in Table 5. The spectrum is listed in Table 13S in the Supporting Information. A total of 58 lines were assigned for the <sup>37</sup>Cl species, whose rotational constants are listed in Table 5. This spectrum is shown in Table 15S in the Supporting Information.

A search was also made for c-type lines because  $\mu_c \sim 2 \times 10^{-30}$  C m. The unperturbed frequencies of these transitions can be rather accurately predicted using the spectroscopic constants of Table 5. However, no c-type transitions were found at their predicted frequencies. The explanation for this is presumed to be the existence of two mirror-image forms of this conformer (see Figures 1 and 2), which indicates that c-type transitions should occur between vibrational states of opposite parity resulting in splitting whose size is twice that of the tunneling frequency. It is not possible to predict the tunneling frequency of II accurately, but it is not expected to be large (in the order of GHz) because tunneling frequencies of related phosphines are just a few megahertz. For example, it is 5.2179(66) MHz in one of the conformers of CH<sub>3</sub>CH<sub>2</sub>PH<sub>2</sub>,<sup>8</sup> and about 10 MHz in the gauche form of H<sub>2</sub>C=CHPH<sub>2</sub>.<sup>13</sup> However, no c-type lines could definitely be assigned, presumably because the c-type

**TABLE 6: Spectroscopic Constants<sup>a</sup> of the First Excited State of the Torsional Vibration of <sup>35</sup>ClCH<sub>2</sub>PH<sub>2</sub>**

<i>A</i> /MHz	24660(20)
<i>B</i> /MHz	3212.406(13)
<i>C</i> /MHz	2957.378(12)
<i>D<sub>J</sub></i> /kHz	1.917(34)
<i>D<sub>JK</sub></i> /kHz	−24.49(42)
<i>D<sub>K</sub></i> /kHz	298.3 <sup>b</sup>
<i>d<sub>1</sub></i> /kHz	−0.25041 <sup>b</sup>
<i>d<sub>2</sub></i> /kHz	−0.00630 <sup>b</sup>
$\Delta^c/10^{-20}$ u m <sup>2</sup>	−6.927(16)
rms <sup>d</sup>	1.746
no. of trans <sup>e</sup>	20

<sup>a</sup> *S*-reduction *F*-representation.<sup>35</sup> Uncertainties represent one standard deviation. Spectrum in Table 14S in the Supporting Information. <sup>b</sup> Fixed. <sup>c</sup> Pseudo inertial defect defined by  $I_c - I_a - I_b$ , where  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia. Conversion factor:  $505\,379.05 \times 10^{-20}$  MHz u m<sup>2</sup>. <sup>d</sup> Weighted root-mean-square deviation. <sup>e</sup> Number of transitions used in the fit.

spectrum is so weak, due to a relatively small  $\mu_c$ , the high energy of rotamer **II**, and because of the quadrupole effect, which splits up the perpendicular c-type transitions to a significant extent.

The value of the pseudo inertial defect of the <sup>35</sup>Cl species of rotamer **II** is  $-6.76033(14) \times 10^{-20}$  u m<sup>2</sup> (Table 5), compared to  $-6.87 \times 10^{-20}$  u m<sup>2</sup> calculated from the MP2 rotational constants shown in Table 2. The pseudo inertial defect of **II**,  $-6.76033(14) \times 10^{-20}$  u m<sup>2</sup>, is less than  $-7.57058(30) \times 10^{-20}$  u m<sup>2</sup> found for rotamer **I** (Table 3). A decrease in the absolute value of the pseudo inertial defect was expected for **II** as compared to **I** due to the orientations of the phosphino group in the two forms, and is additional evidence that the spectrum of **II** has indeed been correctly assigned and not confused with the spectrum of **I**.

Comparison of the experimental rotational constants (Table 5) with the MP2 and B3LYP constants (Table 2) reveals a much better agreement between experiment and theory for the MP2 set of constants. There is good agreement between the theoretical and calculated centrifugal distortion constants.

The substitution coordinates<sup>44,45</sup> of the chlorine nucleus were calculated to be  $|a| = 145.3(2)$  and  $|b| = 18.8(16)$  pm, where the uncertainties have been estimated according to van Eijck.<sup>46</sup> The *c*-coordinate was found to be small and imaginary. These coordinate are close to the MP2 values of  $|a| = 144.6$ ,  $|b| = 18.7$ , and  $|c| = 0.3$  pm.

Twenty a-type transitions of the first excited state of the torsion (Table 14S of the Supporting Information) about the C1–P4 torsion were assigned for the <sup>35</sup>Cl variant; the spectroscopic constants are displayed in Table 6. Relative intensity measurements yielded ca. 175 cm<sup>−1</sup> for this vibration compared to the MP2 harmonic value of 170 cm<sup>−1</sup> (Table 2S, Supporting Information).

The *A* rotational constant of this excited state is not accurate (see Table 5) and an accurate value for the corresponding vibration–rotation constants cannot therefore be calculated. However, the situation is much better for *B* and *C*, whose experimental vibration–rotation constants can be found from Tables 5 and 6 to be  $\alpha_B = 13.46$  and  $\alpha_C = 8.47$  MHz, compared to the B3LYP values of 4.70 and 3.39 MHz, respectively.

**Energy Difference between **II** and **I**.** Relative intensity measurements were made using several <sup>a</sup>R-transitions of conformers **I** and **II** to determine the energy difference between them. The MP2 dipole moment components (Table 2) were used to derive the energy difference, which were calculated according to Townes and Schawlow.<sup>49</sup> It was found that **I** is more stable

than **II** by 4.3(5) kJ/mol. This experimental energy difference is very close to the MP2, 4.0 kJ/mol, and the B3LYP results (4.2 kJ/mol; Table 2).

**Structures.** The fact that the MP2 rotational constants are in better agreement with the experimental rotational constants than the B3LYP constants are, is evidence that the MP2 structure is closer to the equilibrium structure than the B3LYP structure is. The good agreement between the substitution coordinates and the MP2 principal axes coordinates is additional evidence that the MP2 structure is close to the equilibrium structure, which is a general trend.<sup>37</sup>

## Discussion

There are probably several reasons why conformer **I** is the preferred form of ClCH<sub>2</sub>PH<sub>2</sub>. The MP2 distance between the two phosphino group hydrogen atoms and highly electronegative chlorine atom (Pauling electronegativity: 3.16<sup>50</sup>) in **I** is 304 pm. This distance has increased to 319 pm for the nonbonded H6···Cl7 distance and to 401 pm for the nonbonded H5···Cl7 distance in rotamer **II**. The sum of the van der Waals radii<sup>51</sup> of chlorine (180 pm) and hydrogen (120 pm) is 300 pm. Conformer **I** therefore appears to be stabilized by two chlorine–hydrogen interactions, which may be called weak intramolecular hydrogen bonds, whereas only one such bond exists for **II**.

Moreover, the bond moment of the P–H bond is 0.36 Debye<sup>52</sup> with the hydrogen atom at the positive end of the bond, whereas the bond moment of the Cl–C is 1.46 Debye<sup>52</sup> with chlorine as the negative partner. The angle between the Cl–C and P–H bonds in **I** is about 56° according to the MP2 structure. However, the two bonds are oriented in a way that is favorable for electrostatic stabilization.

Electrostatic interactions are not the only effects influencing the conformational composition of ClCH<sub>2</sub>PH<sub>2</sub>. In conformer **I**, the chlorine atom and the lone pair of the phosphorus atom is as far away from one another as they can possibly be, which will minimize repulsion between them. This situation is less favorable in **II**. The more favorable nonbonded interactions in **I** are assumed to be the major reasons why **I** is preferred to **II** by 4.3(5) kJ/mol.

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**Supporting Information Available:** Results of the theoretical calculations (vibrational frequencies, harmonic and anharmonic vibrational fundamentals, vibration–rotation  $\alpha$ -matrix) and the microwave spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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