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Conformational Composition of Cyclopentadienylphosphine Investigated by Microwave Spectroscopy and Quantum Chemical Calculations

Harald Møllendal,*,[†] George C. Cole,[†] and Jean-Claude Guillemin[‡]

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway, and Laboratoire de Synthèse et Activation de Biomolécules, Unité Mixte de Recherche 6052 du Centre National de la Recherche Scientifique, Institut de Chimie de Rennes, Ecole Nationale Supérieure de Chimie de Rennes, F-35700 Rennes, France

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The properties of cyclopentadienylphosphine have been investigated by means of Stark-modulation microwave spectroscopy and quantum chemical calculations at the MP2/aug-cc-pVTZ, B3LYP/6-311++G(d,p), and G3 levels of theory. Spectra attributable to two rotamers denoted conformers I and II have been assigned. Conformer I has a symmetry plane (C_s symmetry) consisting of the bisectors of the cyclopentadiene ring and of the phosphino group with the lone electron pair of phosphorus pointing toward the carbon ring. In conformer II, the phosphino group is rotated approximately 120° out of this plane. Relative intensity measurements have been made, and it was found that conformer II is more stable than I by 1.3(4) kJ/mol. The preferred conformer represents a borderline case of intramolecular hydrogen bond stabilization. The experimental and MP2/aug-cc-pVTZ rotational constants differ by several percent, which indicates that the aug-cc-pVTZ basis set is not large enough to be able to predict an accurate structure for the two conformers that are close to the equilibrium geometries. 5-Substituted 1,3-cyclopentadienyl derivatives may undergo circumambulatory rearrangements. However, there is no manifestation of this effect in the microwave spectrum of cyclopentadienylphosphine.

Introduction

The literature dealing with the gas-phase properties of small aliphatic phosphines is not extensive, because of their toxicity, instability toward air, and their penetrating, unpleasant odors. Microwave (MW) spectroscopy has been employed to investigate CH_3PH_2,[1] $CH_3CH_2PH_2$,[2] $H_2PCH_2CH_2C{\equiv}N$,[3] $HC{\equiv}CPH_2$,[4] $H_2C{=}CHPH_2$,[5,6] $H_2PCH_2CH_2PH_2$,[7] $HC{\equiv}CCH_2PH_2$,[8] $H_2C{=}CH\text{-}CH_2PH_2$,[9] $H_2C{=}C{=}CHPH_2$,[10] and cyclopropylmethylphosphine ($C_3H_5CH_2PH_2$).[11] These studies have shown that phosphines have unique physical properties.

One aspect of some of these investigations has been to explore whether the phosphino group is capable of acting as a proton donor in the formation of weak intramolecular hydrogen (H) bonds. This was an important motivation for performing the MW studies of $H_2PCH_2CH_2C{\equiv}N$,[3] $H_2PCH_2CH_2PH_2$,[7] $HC{\equiv}CCH_2PH_2$,[8] $H_2C{=}CHCH_2PH_2$,[9] and $C_3H_5CH_2PH_2$.[11] More than one rotameric form was observed for each of these five compounds. In four of these cases, $H_2PCH_2CH_2C{\equiv}N$, $HC{\equiv}CCH_2PH_2$, $H_2C{=}CHCH_2PH_2$, and $C_3H_5CH_2PH_2$, the lowest-energy conformation is also that in which conditions for forming an internal H bond are most favorable. The phosphino group interacts with π-electrons in the first three molecules, and with the pseudo-π electrons[12] of the cyclopropyl ring in the last example. In the present work, studies of the properties of aliphatic phosphines are extended to include cyclopentadienylphosphine (CPP), $C_5H_5PH_2$, where H bonding might be possible in one of its conformations.

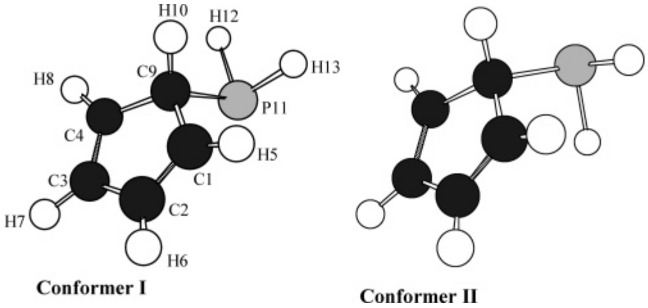

Figure 1. The two preferred conformers of cyclopentadienylphosphine. The orientation of the phosphino group is different in the two conformers. Conformer I has a symmetry plane consisting of the H10−C9−P11 link of atoms and the bisectors of the cyclopentadiene ring and of the phosphino group. In conformer II, which has no symmetry, the phosphino group is rotated through approximately 120° from this plane. Conformer II is more stable than conformer I by 1.3(4) kJ/mol and possibly stabilized by an internal hydrogen bond interaction between C1C2 double bond and H12 and H13.

High-level quantum chemical calculations[13,14] indicate that there are two minima on the potential energy hypersurface of CPP corresponding to conformers I and II, which are depicted in Figure 1. Conformer I has a symmetry plane (C_S symmetry) formed by the C9H10 bond and the bisector of both the cyclopentadienyl ring and the phosphino group. In conformer II, the phosphino group is rotated by approximately 120° about the C9P11 bond relative to its position in conformer I. This brings both hydrogen atoms of the phosphino group into proximity with the C1C2 double bond, which is a prerequisite for hydrogen bonding.

There is a second reason for undertaking this research. The title compound is a 5-substituted 1,3-cyclopentadienyl derivative

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* Corresponding author. Phone: +47 2285 5458. Fax: +47 2285 5441. E-mail: harald.mollendal@kjemi.uio.no.

[†] University of Oslo.

[‡] Ecole Nationale Supérieure de Chimie de Rennes.

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with a heteroatom (phosphorus) attached to the allylic carbon atom via a σ-bond. Such compounds are subject to circumambulatory (walk) rearrangement caused by rapid migration of substituents, which make them particularly interesting.[13−16] This unique fluxional phenomenon is in many cases easily observed by NMR spectroscopy via the temperature dependence of chemical shifts.[17−20] Numerous 5-substituted 1,3-cyclopentadienyl derivatives have therefore been prepared to study this effect. Experimental and theoretical investigations of circumambulatory behavior have been reported for silicon,[19,21−23] germanium,[19,23−25] phosphorus,[13−16,26] and arsenic[27,28] derivatives.

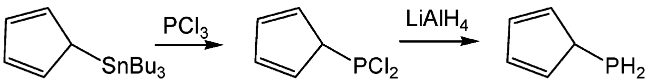
The title compound, which was recently synthesized,[13] has also been the subject of such an investigation.[13] Photoelectron spectroscopy, mass spectrometry, and quantum chemical calculations were also performed in this study. The Gibbs' energy ($\Delta G^{\ddagger}$) for the barrier height of the circumambulatory rearrangement was calculated to be about 87 kJ/mol (B3LYP/6-311+G(d,p) level of theory). A sufficiently low barrier to rearrangement should lead to anomalies in the MW spectrum.

MW spectroscopy is ideally suited to investigate both conformational equilibria and a low-barrier circumambulatory behavior through its superior accuracy and resolution. High-level quantum chemical calculations have been made to support and guide the experimental work.

Experimental Section

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

CPP has been synthesized by reduction of the corresponding cyclopentadienyldichlorophosphine.



Synthesis of Cyclopentadienyldichlorophosphine.[13,29] In a two-necked flask equipped with a nitrogen inlet and a stirrer bar was introduced PCl_3 (13.8 g, 0.1 mol). The flask was immersed in a bath cooled to −30 °C, and the cyclopentadienyltributylstannane (35.6 g, 0.1 mol) was introduced dropwise for 10 min. At the end of the addition, the bath was removed and the solution was stirred for 10 min at room temperature. The cyclopentadienyldichlorophosphine was purified by distillation employing a vacuum line and selective condensation in a trap cooled at −40 °C under 0.1 mbar. Yield: 11.4 g, 68%. After addition of degassed tetraglyme (50 mL) under nitrogen, the solution can be kept for months in a freezer (−30 °C).

Synthesis of Cyclopentadienylphosphine.[13] The apparatus previously described for the preparation of propargylphosphine was used.[8] In a 250 mL two-necked flask were introduced the reducing agent $LiAlH_4$ (1.0 g, 25 mmol) and tetraglyme (30 mL). The flask was attached to the vacuum line equipped with two cold traps. The flask was cooled (−20 °C) and degassed. The cyclopentadienyldichlorophosphine (1.67 g, 10 mmol) diluted in tetraglyme (10 mL) was then slowly introduced with a microsyringe or a flexible needle. To limit oligomerization, CPP was distilled off in vacuo from the reaction mixture during the course of the addition of dichlorophosphine. High-boiling impurities were selectively condensed in a cold trap (−40 °C), and CPP was selectively condensed in a cold trap cooled at a precise temperature of −75 °C under 0.1 mbar to remove low boiling impurities (PH_3 and cyclopentadiene). At the end of the reaction, this second trap was disconnected from the vacuum line by stopcocks. CPP (0.51 g, 5.2 mmol) was obtained in a 52% yield and kept in dry ice before analysis by MW spectroscopy. Addition under nitrogen of degassed tetraglyme (20 mL) to the phosphine allows this solution to be kept in a freezer (−30 °C) for several weeks.

Stark Spectrometer Experiment. The MW spectrum of CPP was studied using the Oslo Stark spectrometer.[30] The upper frequency limit available for this spectrometer has now been extended from 62 to about 81 GHz with the addition of a AMC-15-RF000 frequency quadrupler and a DXP-15-RPFW0 detector (Millitech). Measurements were made in the 22−81.2 GHz spectral range. The MW brass cell was cooled to about −30 °C during the experiments. Lower temperatures would have increased the spectral intensity, but it was not possible to go below the said temperature, because of insufficient vapor pressure of CPP. The spectrum was measured at a gas pressure of roughly 10 Pa and a Stark modulation field strength of about 1100 V/cm. This field strength is sufficient to modulate most transitions. The spectrum was recorded electronically using a LabView-program by Grønås.[31] The spectrum is comparatively weak, and the experimental accuracy associated with rotational transition frequencies is therefore estimated to be of the order of ±0.15 MHz.

CPP easily oligomerizes or polymerizes. Several samples, each consisting of a few milligrams of CPP, were used. The samples were kept in dry ice (−78 °C) when not in use. The samples were not found to react over the course of several days. The compound slowly reacted in the brass cell employed in this experiment, presumably because of an oligomerization reaction, and therefore the cell had to be refilled with fresh sample every few hours.

Results

Quantum Chemical Calculations. The Gaussian 03 program package[32] running on the HP superdome in Oslo was used to perform the quantum chemical calculations. To facilitate the spectral assignments of a complicated MW spectrum, it is important to have the most accurate predictions of the rotational constants possible.

It has been claimed[33] that Møller−Plesset second-order perturbation calculations[34] employing a large basis set predict an accurate equilibrium structure. The rotational constants calculated from this structure are generally close to the effective rotational constants derived from the MW spectra. Dunning's comparatively large correlation-consistent triple-ζ basis set, aug-cc-pVTZ,[35] with polarized valence electrons augmented with diffuse functions, was therefore chosen. The frozen-core approximation was employed in these MP2/aug-cc-pVTZ calculations. The structures of conformers I and II were fully optimized with no symmetry restrictions imposed in the case of I. The rotational constants, dipole moments, and energy differences obtained in these calculations are given in Table 1. The MP2 and experimental rotational constants are compared below. It was found that an unexpectedly large difference exists between them. This must originate from the predicted structure. Details of the MP2 structure are therefore not given here, but instead listed in Table 5S in the Supporting Information.

It should be noted that the present MP2 calculations are so large that vibrational frequencies were not calculated, because of restrictions on computer time. The ordinary test that only positive vibrational frequencies are obtained for minima on the potential energy hypersurface could therefore not be employed, but it is considered highly likely that only positive values would have been obtained, if such calculations had been performed.

It is also useful to have good estimates of the vibrational frequencies, the centrifugal distortion constants, and the vibra-

TABLE 1: Calculated Rotational Constants, Centrifugal Distortion Constants, Dipole Moments, and Energy Differences of Conformers I and II of Cyclopentadienylphosphine

	I		II	
	MP2	B3LYP	MP2	B3LYP
Rotational Constants (MHz)				
A	6107.2	6351.0	6311.5	6467.0
B	2334.5	2184.1	2234.5	2132.6
C	1974.6	1837.2	1885.6	1794.1
Centrifugal Distortion Constants^a (kHz)				
Δ_J		0.78		0.58
Δ_{JK}		−3.4		−2.4
Δ_K		9.9		8.4
δ_J		0.039		0.031
δ_K		0.40		0.43
Dipole Moment^b (10^{-30} C m)				
μ_a	0.6	0.4	2.0	1.4
μ_b	0.0^c	0.0^c	2.0	1.9
μ_c	3.1	3.2	0.4	0.5
μ_{tot}	3.2	3.2	2.9	2.5
Energy Difference^d (kJ/mol)				
	0.0	+1.2	+0.7	0.0

[a] Watson A-reduction.[38] Not available from the MP2 calculations; see text. [b] 1 D = 3.33564×10^{-30} C m. [c] For symmetry reasons. This conformer has C_s symmetry. [d] Relative to conformer I. The MP2 energy differences have not been corrected for zero-point vibrational energies, whereas the B3LYP energy differences have; see text.

tion−rotation interaction constants. The calculations of these parameters have been made using a less advanced quantum chemical procedure, again because of computational restrictions. In this case, DFT calculations employing the B3LYP functional[36,37] and the 6-311++G(d,p) basis set were performed with no restrictions on symmetry. The geometry obtained in these calculations is shown in the Supporting Information, Table 5S. The B3LYP rotational constants, dipole moments, Watson's A-reduction quartic centrifugal distortion constants,[38] and energy differences are listed in Table 1.

It is seen in this table that the predictions of some of the components of the dipole moment along the intertial axes vary considerably. For example, the MP2 value of the μ_a dipole moment component of conformer II is 2.0×10^{-30} C m, as compared to the B3LYP prediction being 1.4×10^{-30} C m.

The use of quantum chemical calculations to estimate the energy differences between conformers is another source of useful information. The MP2 calculations predict that conformer I is 0.7 kJ/mol more stable than II, with no corrections for zero-point vibrational energies being made. This is reversed in the B3LYP computations, where I is predicted to be 1.2 kJ/mol less stable than II. Corrections for zero-point vibrational energies have been included in this energy difference. The G3 procedure[39] is renowned for predicting accurate energy differences. G3 calculations were therefore performed, and an energy difference of 0.3 kJ/mol was obtained, with conformer II as the more stable.

MW Spectrum and Assignment of the Ground Vibrational State of Conformer II. The absolute intensities of MW transitions are proportional to the squared dipole moment component along a principal inertial axis and inversely proportional to the partition function. The partition function at −30 °C is large for both rotameric forms. Moreover, the dipole moment components are not larger than approximately 3×10^{-30} C m for either of them according to the calculations (Table 1).

TABLE 2: Spectroscopic Constants^a of the Ground and of the First Vibrationally Excited State of the Lowest Bending Vibration of Conformer II of Cyclopentadienylphosphine

vibrational state	ground	first excited bending
A (MHz)	6408.9846(31)	6410.9551(42)
B (MHz)	2179.9538(10)	2179.5541(16)
C (MHz)	1831.4096(10)	1831.5286(16)
Δ_J (kHz)	0.6432(19)	0.6240(31)
Δ_{JK} (kHz)	−2.7123(23)	−2.4967(39)
Δ_K (kHz)	8.656(43)	7.989(64)
δ_J (kHz)	0.032142(98)	0.03179(14)
δ_K (kHz)	0.4664(44)	0.4572(66)
rms^b (MHz)	0.136	0.148
max J^c	62	58
no transitions^d	424	259

[a] A-reduction I^r-representation.[38] Full spectra are given in the Supporting Information. Uncertainties represent one standard deviation. [b] Root-mean-square deviation. [c] Maximum value of J. [d] Number of transitions.

Conformer I is predicted to have a sizable dipole moment component along the c-inertial axis, whereas II has a sizable μ_b. The perpendicular b- and c-type spectra are very rich at this temperature for a molecule having $A \approx 6.4$, $B \approx 2.2$, and $C \approx 1.9$ GHz. A dense and comparatively weak spectrum was expected for these reasons, and this was also found to be the case. In fact, absorption lines occur every few MHz throughout the entire MW region.

The quantum chemical calculations indicate that there is a small energy difference between the two forms. Conformer II is predicted to have $\mu_a \approx 2 \times 10^{-30}$ C m. ^{a}R-transitions are often comparatively easy to assign, and searches for them were first made using a prediction based on the MP2 rotational constants and the B3LYP centrifugal distortion constants given in Table 1. These transitions were readily found relatively close to the predicted frequencies. Fairly accurate rotational constants were obtained from the least-squares fit of these a-type transitions. The assignment of the b-type R-branch and Q-branch lines was then straightforward. The fit was gradually extended to include about 450 transitions with a maximum value of $J = 62$. The frequencies of the c-type transitions could then be predicted with a high degree of accuracy. However, no c-type lines were identified presumably because of insufficient intensities. It is seen in Table 1 that μ_c is predicted to be small, and this is assumed to be the reason that these transitions were not found, because their intensities are proportional to μ_c^2.

The full spectrum of II is given in Table 1S in the Supporting Information. The spectroscopic constants (Watson's A-reduction I^r- representation[38]) obtained in a least-squares fit of 424 transitions (199 a-type and 225 b-type) using Sørensen's Rotfit program[40] are given in Table 2. Only quartic centrifugal distortion constants were fitted, because the resulting fit has a root-mean-square deviation of 0.136 MHz, which is comparable to the experimental uncertainty of ±0.15 MHz. Inclusion of sextic centrifugal distortion constants did not improve the fit significantly, and they have therefore been omitted.

The differences between the effective (Table 2) and the MP2 rotational constants (Table 1) are +1.52%, −2.44%, and −2.96% for A, B, and C, respectively. This is larger than expected for the difference between effective rotational constants and the equilibrium rotational constants (roughly 1%) and indicates that the MP2 structure in Table 5S is not very close to the true equilibrium structure. The aug-cc-pVTZ basis set is obviously too small to produce a near-equilibrium structure for this compound within the MP2 approximation.[33]

The differences between the experimental and calculated (B3LYP) quartic centrifugal distortion constants are +9.9%, −12.5%, +3.7%, +3.2%, and +8.2% for Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K, respectively, which is considered satisfactory.

It was not possible to measure the dipole moment of the two rotamers, as the intensity of the low-J lines normally used for this purpose was too low.

It was mentioned above that circumambulatory rearrangement occurs for cyclopentadienyl derivatives. However, there is no evidence of this large-amplitude motion in the MW spectrum of either of the two conformers of CPP. This is not surprising, because the barrier height has been estimated to be as high as 87 kJ/mol,[13] which would not lead to splitting of lines or other spectral anomalies.

It is seen in Table 1 that the rotational constants of conformers I and II are rather similar. Rotational constants alone cannot therefore be used to unambiguously identify a rotamer. However, the components of the dipole moment along the principal inertial axes are predicted to be very different. Conformer I has its major component along the c-axis, while II has its major components along the a- and b-axes (Table 1). The fact that only a- and b-type lines were observed is taken as conclusive evidence that the spectrum of II has indeed been assigned and not confused with I.

Vibrationally Excited State of Conformer II. The ground-state lines of this form were accompanied by several satellites, which presumably belong to vibrationally excited states. About 280 transitions of the spectrum of the most intense vibrationally excited state were assigned. The spectroscopic constants derived from 259 of them are listed in Table 2; the full spectrum is found in the Supporting Information, Table 2S. Relative intensity measurements yielded 123(30) cm^{-1} for this vibration as compared to the B3LYP value of 135 cm^{-1}. This vibration is the lowest bending mode.

The spectroscopic vibration−rotation constant α_X is given by $\alpha_X = X_0 - X_1$, where X_0 is the X rotational constant in the ground vibrational state and X_1 is the corresponding constant of the first excited state of a normal vibration.[41] The values of the α_X's calculated from the entries in Table 2 are $\alpha_A = -1.98$, $\alpha_B = +0.40$, and $\alpha_C = -0.12$ MHz, which compare favorably with the corresponding values, −0.76, +0.39, and −0.14 MHz, obtained from the B3LYP calculations.

Assignment of Conformer I. This rotamer is seen (Table 1) to have the major component of its dipole moment along the c-inertial axis, while μ_b is zero for symmetry reasons and μ_a is quite small. It was therefore decided to attempt to assign c-type lines first as the first step.

The ^{c}Q-transitions are normally easier to assign than the ^{c}R-transitions. Searches were therefore made for the low-J members of the $K_{-1} = 7 \leftarrow 6$ transitions, which were predicted to occur in the vicinity of 57 GHz, to form a recognizable pattern, and to be well modulated at relatively low Stark fields. This series was found after some searching. Further ^{c}Q-transitions were then gradually included in the least-squares fit. The B3LYP quartic centrifugal distortion constants were helpful in this procedure. The ^{c}R-transitions were next identified using a trial and error procedure. Ultimately, 220 c-type transitions were identified with a maximum value of $J = 65$. No transitions attributable to a- or b-type lines could be identified, although it is assumed that their hypothetical frequencies could be predicted very accurately. Two hundred c-type transitions, given in the Supporting Information Table 3S, were used to derive the spectroscopic constants listed in Table 3. One sextic centrifugal distortion constant, ϕ_J, was included in the fit in this case.

TABLE 3: Spectroscopic Constants[a] of the Ground and of the First Vibrationally Excited State of the Lowest Bending Vibration of Conformer I of Cyclopentadienylphosphine

vibrational state	ground	first excited bending
A (MHz)	6271.5364(30)	6271.3298(62)
B (MHz)	2244.4384(13)	2245.5138(37)
C (MHz)	1886.2355(13)	1887.8788(39)
Δ_J (kHz)	0.90064(85)	0.8658(43)
Δ_{JK} (kHz)	−4.0018(39)	−3.695(13)
Δ_K (kHz)	10.532(15)	9.566(94)
δ_J (kHz)	0.04164(22)	0.04051(61)
δ_K (kHz)	0.469(11)	0.396(36)
ϕ_J[e] (Hz)	0.000217(19)	−[f]
rms[b] (MHz)	0.164	0.148
max J[c]	65	46
no transitions[d]	200	82

[a−d] Comments as for Table 2. [e] Further sextic constants preset at zero. [f] Preset at zero.

The differences between the effective (Table 3) and the MP2 rotational constants (Table 1) are +2.61%, −4.01%, and −4.68% in the cases of A, B, and C, respectively. These differences are even larger than those found for conformer II. It is in fact an unusually large difference considering the high computational level (MP2/aug-cc-pVTZ) employed to predict the structure of this rotamer. Obviously, the aug-cc-pVTZ basis set is not large enough to predict near equilibrium structures in either of these two cases.[33]

The differences between the experimental and calculated (B3LYP) quartic centrifugal distortion constants are +13.4%, −14.3%, +5.9%, +6.7%, and +15.4% for Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K, respectively.

The first excited state of the lowest bending vibration was assigned for this rotamer. Eighty-two transitions with $J_{\max} = 46$ were used to determine the spectroscopic constants shown in Table 3. The transitions employed in this case are listed in Table 4S in the Supporting Information. Relative intensity measurements yielded 111(30) cm^{-1} for this vibration, as compared to 125 cm^{-1} (B3LYP value). The values of the vibration−rotation constants (the α_X's) calculated from the entries in Table 3 are $\alpha_A = 0.21$, $\alpha_B = -1.07$, and $\alpha_C = -1.64$ MHz, which differ significantly from the corresponding values from the B3LYP calculations, 7.08, −3.04, and −3.51 MHz.

Energy Difference. The internal energy difference between conformers I and II has been derived using a variant of eq 3 of Esbitt and Wilson.[42] According to Wilson,[43] the internal energy difference is given by

$$E''_{v''} - E'_{v'} = E'_{J'} - E''_{J''} + RT \ln L \tag{1}$$

where $E''_{v''}$ and $E'_{v'}$ are the internal energies of the two conformers in the v'' and v' vibrational states, respectively, $E'_{J'}$ and $E''_{J''}$ are the lowest energy levels of the two rotational transitions under investigations, R is the universal gas constant, and T is the absolute temperature. L is given by

$$L = \frac{S'}{S''}\,\frac{g''}{g'}\left(\frac{v''\mu''}{v'\mu'}\right)^2 \frac{l''}{l'}\,\frac{\Delta v'}{\Delta v''}\,\frac{\lambda''}{\lambda'}\,\frac{(2J'+1)}{(2J''+1)} \tag{2}$$

where S is the peak signal amplitude of the radiation unsaturated line, g is the degeneracy other than the rotational degeneracy, which is $2J + 1$, v is the frequency of the transition, μ is the principal-axis dipole moment component, l is the radiation wavelength in the Stark cell,[44] Δv is the line breadth at half-height, λ is the line strength, and J is the principal rotational quantum number.

The internal energy difference between the ground vibrational states of conformers I and II was determined by comparing the intensities of three selected ground-state transitions of each conformer. The lines employed in this comparison procedure were relatively strong *c*-type Q-branch lines of I and *b*-type Q-branch lines of II. These transitions were not detectably overlapped by other lines. The frequency differences of the pairs of transitions that were compared were less than 60 MHz to minimize variations in reflections within the MW cell. The statistical weight (g) of conformer I was assumed to be 1, whereas the statistical weight of II was assumed to be 2. The radiation wavelengths (l) were assumed to be identical. The ratio of the dipole moment components of the two forms was calculated using the MP2 predictions in Table 1.

The internal energy difference, $E_{II} - E_I$, obtained this way varied between −1.1 and −1.5 kJ/mol (conformer II more stable than I). The average value was found to be $E_{II} - E_I = -1.3$ kJ/mol. There are several sources of errors in this procedure. One standard deviation has been conservatively estimated to be ±0.4 kJ/mol by evaluating the uncertainties associated with the many parameters of eq 2.

The fact that conformer II is 1.3(4) kJ/mol more stable than I should be compared with the theoretical results. The B3LYP prediction of this energy difference (Table 1) is closest ($E_{II} - E_I = -0.7$ kJ/mol), followed by G3 (−0.3 kJ/mol), and finally by MP2 (+1.2 kJ/mol).

Discussion

The conformational composition of CPP is certainly a compromise of several forces. Conformer I has a geometry that is ideal for interaction of the lone electron pair of phosphorus with the electrons of the carbon ring. This effect may be quite important for the stability of I.

Conformer II has a geometry that brings both the phosphino group hydrogen atoms H12 and H13 into close proximity with the C1C2 double bond. The distances from H12 and H13 to C1 are estimated to be approximately 288 and 279 pm, respectively. The sum of the van der Waals radii of aromatic carbon (170 pm) and hydrogen (120 pm) is 290 pm.[45] This supports the assumption that a very weak intramolecular hydrogen bond interaction may indeed stabilize conformer II and may be a major reason that II is preferred to I.

Formally, the C2−C1−C9−P11 and C3−C3−C9−P11 links of atoms are similar to the corresponding chain of atoms in allyphosphine. Three rotameric forms were identified in allylphosphine.[9] Interestingly, the most stable rotameric form of allylphosphine corresponds to conformer II.

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Supporting Information Available: MW spectra of the two rotameric forms of CPP. This material is available free of charge via the Internet at http://pubs.acs.org.

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