# Synthesis, Microwave Spectrum, Quantum Chemical Calculations, and Conformational Composition of the Novel Compound Cyclopropylethylidynephosphine (C₃H₅CH₂C≡P)

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Ⓢ *Supporting Information*

ABSTRACT: The synthesis of the novel compound cyclopropylethylidynephosphine (C₃H₅CH₂C≡P) and its microwave spectrum are reported together with quantum chemical calculations. The spectrum, which reveals the existence of two conformers, has been recorded in the 38−109 GHz spectral range at room temperature. The H−C−CH₂−C chain of atoms is *synclinal* in one rotamer denoted **sc**, and *antiperiplanar* in the second conformer called **ap**. The spectra of the ground vibrational state and two vibrationally excited states were assigned for each rotamer. The vibrational frequencies of these excited states were determined by relative intensity measurements. Relative intensity measurements were also conducted to determine the energy difference between **ap** and **sc**. The latter conformer was found to be the lower-energy form and $E_{ap} - E_{sc}$ was determined to be 0.9(4) kJ/mol. The microwave study has been augmented by quantum chemical calculations at the CCSD/cc-pVQZ and MP2/cc-pVTZ levels of theory. The CCSD predictions were generally in good agreement with experiment, while somewhat mixed results were obtained in the MP2 calculations.
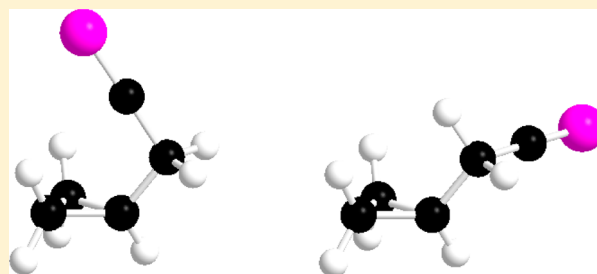
INTRODUCTION

The phosphaalkyne (alkylidynephosphine) group, C≡P, is a relatively "new" functional group. The first phosphaalkyne was discovered as late as in 1961, when Gier[1] produced HC≡P, by passing phosphine through a specially constructed carbon arc. A microwave (MW) study by Tyler[2] three years later showed that the structure of the compound detected by Gier is undoubtedly HCP, and not HPC. Several small phosphaalkynes, for example, FC≡P,[3] CH₃C≡P,[4] HC≡CC≡P,[5] N≡CC≡P,[6] N≡CC≡ CC≡P,[7] H₂C=CHC≡P,[8] CF₃C≡P,[9] and C₆H₅C≡P,[10] were produced in the 70s and 80s mainly by pyrolysis of suitable precursor compounds, and their structures were confirmed by MW spectroscopy. These early studies demonstrated that HC≡P is not a chemical oddity, but in fact the simplest representative of the new phosphaalkyne functional group.

It was soon established that phosphaalkynes are useful synthons.[11] New ways of producing them other than pyrolysis were also developed.[11] A convenient synthesis of phosphaalkynes, also used to produce the title compound, is based on the remarkable acidity of hydrogens on the phosphorus atom of 1-alkynylphosphines, RC≡CPH₂. These compounds are readily converted to the corresponding phosphaalkynes, RC≡P, in a solvent using a Lewis base (DBU) or in the gas phase by reaction with a solid base (K₂CO₃).[12] Phosphaalkyne synthons produced in this or in alternative manners have been used extensively in the

last 25 years and have led to a rapid development of phosphorus chemistry.[11−19]

The gas-phase structures of the several small phosphaalkynes referred to above were determined by MW spectroscopy. Very few, if any, conformational gas-phase studies by this method have been reported in the past. Conformational studies are desirable to better understand the chemical behavior of members of a particular functional group. We have therefore synthesized cyclopropylethylidynephosphine (C₃H₅CH₂C≡P), which in principle should be capable of exhibiting rotational isomerism. This compound is a methylcyclopropyl derivative, C₃H₅CH₂X, and rotation about the C₃H₅−CH₂ bond could result in two rotameric forms. In one of these, the H−C−C−X link of atoms is antiperiplanar (*ap*, dihedral angle = 180°), whereas the second conformer has a synclinal (*sc*, dihedral angle ≈ 60°) conformation for this chain. Many C₃H₅CH₂X compounds including X = F,[20−24] Cl,[21,25−28] Br,[21,26,28,29] I,[21,30] OH,[31] SH,[32] SeH,[33] NH₂,[34] PH₂,[35] CH₃,[36] SiH₃,[37−40] SiF₃,[37,41,42] C≡N,[43,44] C≡C−H,[45,46] and N≡C[47] have been investigated by microwave (MW), infrared (IR), and/or Raman spectroscopy in the past often in conjunction with quantum chemical calculations.

The energy differences between *sc* and *ap* conformers of these molecules have been determined in most cases and found to vary considerably. However, *sc* forms are found to be the lower-energy form in all these compounds with one exception, namely, $C_3H_5CH_2C\equiv CH$,[45] where the *ap* conformer is 0.77(33) kJ/mol lower in energy than the *sc* form.[45] Another compound also having a triple-bonded X-substituent, $C_3H_5CH_2N\equiv C$,[47] is a borderline case, where $E_{ap} - E_{sc} = 0.2(7)$ kJ/mol.[47] The *sc* rotamer is the lower-energy conformer in the corresponding nitrile, $C_3H_5CH_2C\equiv N$.[43,44] The nitrogen atom of $C_3H_5CH_2C\equiv N$ and the phosphorus atom of $C_3H_5CH_2C\equiv P$ both belong to main group 15. An interesting question is whether the conformational properties of $C_3H_5CH_2C\equiv P$ will resemble those of $C_3H_5CH_2C\equiv N$, or will the phosphaalkyne be similar to the two other molecules with a triple-bonded X-substituent, $C_3H_5CH_2C\equiv CH$ and $C_3H_5CH_2N\equiv C$.

In Figure 1, models of the two forms, denoted **ap** and **sc**, of cyclopropylethylidynephosphine, which will henceforth be
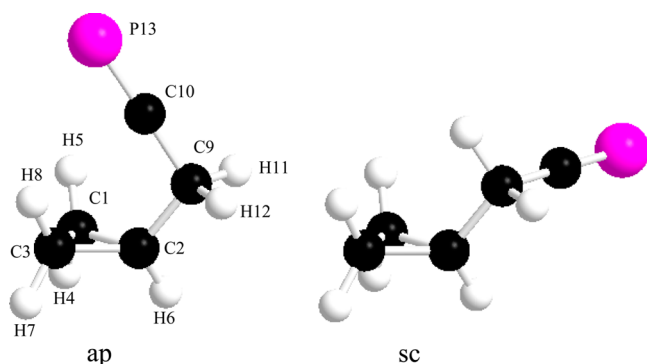

Figure 1. Models of the H6−C2−C9−C10 antiperiplanar (**ap**) and synclinal (**sc**) conformers of cyclopropylethylidynephosphine. The MW spectra of these two forms were assigned and **sc** was found to have a 0.9(4) kJ/mol lower energy than **ap** from relative intensity measurements.

referred to as CEP, are displayed with atom numbering indicated on **ap**. The H6−C2−C9−C10−P13 atoms form a symmetry plane that bisects the cyclopropyl ring of **ap**, which has C_S symmetry, while **sc** has no symmetry. A mirror image form with identical spectroscopic properties exists for **sc**, which therefore has a statistical weight of 2 relative to the statistical weight of **ap**, which is 1.

MW spectroscopy was chosen as our experimental method due to its superior accuracy and resolution, which is ideal for conformational studies. Another advantage of this method is that fairly accurate energy differences between conformers can be determined from relative intensity measurement. The experimental work was augmented by quantum chemical modeling at high methodological levels because parameters that are very useful for the assignment of the MW spectrum are obtained in this manner. These calculations also provide parameters that are not readily available from experiments but can be used advantageously together with experimental data to understand better the chemical problem under consideration.

■ EXPERIMENTAL SECTION

Synthesis of CEP. Cyclopropylethynylphosphine[48] (196 mg, 2.0 mmol) was slowly vaporized in a vacuum line over solid potassium carbonate (42 g, 0.3 mol) heated to 300 °C in vacuum gas solid reaction (VGSR) conditions.[49] CEP was formed

(Scheme 1) by a base-induced rearrangement on the carbonate and condensed in a trap immersed in a −100 °C cold bath. Yield:

Scheme 1
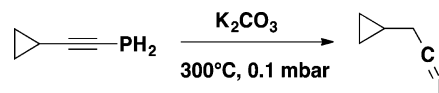
120 mg, 61%. (for similar experiments, see ref 12). $\tau_{1/2}$ (5% in $CDCl_3$ at 20 °C): 30 h.

^1H NMR ($CDCl_3$, 400 MHz) δ: 0.26 (m, 2H, 1 H of each c-CH_2), 0.49 (m, 2H, 1H of each c-CH_2), 0.97 (m, 1H, $^3J_{HH}$ = 6.2 Hz, CH), 2.40 (dd, 2H, $^3J_{PH}$ = 14.7 Hz, $^3J_{HH}$ = 6.2 Hz, CH_2CP). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 4.1 ($^1J_{CH}$ = 159.2 Hz (t), c-CH_2); 10.4 ($^1J_{CH}$ = 160.7 Hz (d), $^3J_{CP}$ = 8.0 Hz, CH); 33.8 ($^2J_{CP}$ = 19.6 Hz (d), $^1J_{CH}$ = 130.6 Hz (t), CH_2); 174.1 ($^1J_{CP}$ = 44.3 Hz (d), CP). ^{31}P NMR ($CDCl_3$, 160 MHz) δ: −58.8 ($^3J_{PH}$ = 14.7 Hz (t)). IR (gas phase, ν, cm^{-1}): 3091 (m), 2969 (vs), 2897 (vs), 2863 (vs), 1541 (m, ν_{CP}), 1462 (m), 1370 (m), 1202 (m), 1131 (vs), 1033 (m), 881 (m). (vs, very strong; s, strong; m, medium).

Spectroscopic Experiments. CEP is a colorless liquid with a vapor pressure of roughly 100 Pa at room temperature. The sample was kept in a freezer at −80 °C or in liquid nitrogen when not in use. The sample was allowed to warm up to room temperature in order to fill the MW cell with fresh sample. Rapid polymerization and formation of a brownish product was seen for the liquid at room temperature, so the liquid sample was cooled down by dry ice or liquid nitrogen immediately after the cell had been filled. Its MW spectrum was recorded at room temperature at a pressure of 5−10 Pa. No degradation of the sample in the cell was observed at these low vapor pressures. The MW spectrum was studied with 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.[50] 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 spectrum was investigated in the whole 38−109 GHz frequency interval. Radio-frequency microwave double-resonance experiments (RFMWDR), similar to those of Wodarczyk and Wilson,[51] were also conducted to unambiguously assign particular transitions, using the equipment described elsewhere.[50]

■ RESULTS AND DISCUSSION

Quantum Chemical Calculations. The present frozen-core MP2[52] and CCSD[53−56] calculations were performed employing the Gaussian 09[57] and Molpro[58] programs running on the Abel cluster in Oslo. Dunning's[59] correlation-consistent cc-pVTZ triple-ζ basis set was used in the MP2 computations, and the cc-pVQZ quadruple-ζ basis set[59] was employed in the CCSD calculations. The default convergence criteria of the two computer programs were observed.

A MP2/cc-pVTZ potential function for rotation about the C2−C9 bond was calculated using the scan option of Gaussian 09. The H6−C2−C9−C10 dihedral angle was stepped in 10° intervals in these calculations while all other structural parameters were allowed to vary freely. The function is drawn in Figure 2. The function has two minima corresponding to **ap** (180°) and **sc** (≈62°).

The optimized structures, dipole moments, harmonic and anharmonic vibrational frequencies, the quartic and sextic Watson centrifugal distortion constants,[60] the vibration−
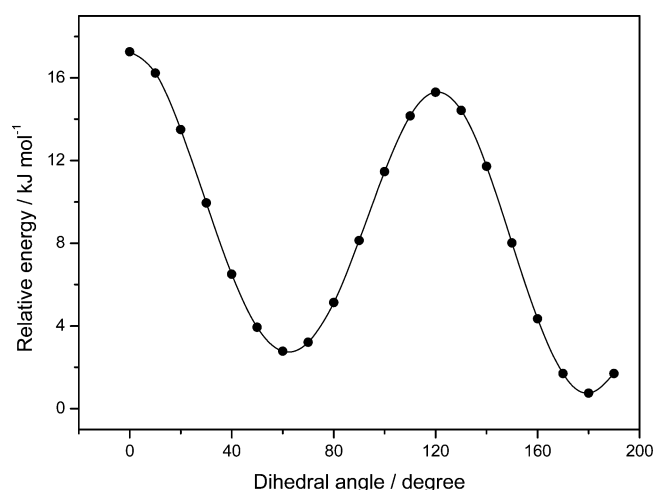
Figure 2. Relative MP2/cc-pVTZ electronic energy as a function of the H6−C2−C9−C10 dihedral angle. The function has minima at 62.3 (**sc**) and 180.0° (**ap**) and maxima at 0 and 120.8°. **ap** represents the global energy minimum with an electronic energy that is 2.00 kJ/mol less than the energy of **sc**. The energies of the two maxima are 16.54 (0°) and 14.02 kJ/mol (120.8°) relative to the energy of **ap**. (Note that the MP2 prediction that **ap** has a lower electronic energy than **sc** is in disagreement with experiment, where it is found that the internal energy of **sc** is lower by 0.9(4) kJ/mol; see text).

rotation constants (the α's),[61] and the differences between the equilibrium and the effective ground-state rotational constants of **sc** and **ap** were obtained from the MP2 calculations. The centrifugal distortion constants and the α's were calculated as described by McKean et al.[62] The results are given in Table 1S (**ap**) and 2S (**sc**) of the Supporting Information.

The H6−C2−C9−C10 dihedral angle is 62.3° in **sc** (Table 2S) and exactly 180° in **ap** (Table 1S) according to the MP2 computations and the electronic energy difference between these two rotamers is 2.00 kJ/mol favoring **ap**. This energy difference becomes 1.66 kJ/mol after correction for zero-point vibrational effects (Tables 1S and 2S). The maxima (transition states) are found at exactly 0°, 16.54 kJ/mol above the **ap** minimum, and at 120.8°, 14.02 kJ/mol above the **ap** minimum.

Finally, comprehensive CCSD/cc-pVQZ calculations of optimized structures, dipole moments and electronic energies of **ap** and **sc** were performed using the MP2 structures in Tables 1S and 2S as starting points. **ap** was assumed to have a symmetry plane in these calculations to save computational time. Unfortunately, it is not possible to calculate vibrational frequencies and centrifugal constants at the CCSD level given our present computational resources.

The resulting CCSD structures, electronic energy difference, and dipole moments are shown in Table 1. Further structural details are displayed in Table 3S (**ap**) and 4S (**sc**) of the Supporting Information. The rotational constants obtained from the CCSD structures are listed together with their experimental equivalents in the last columns of Tables 2 (**sc**) and 3 (**ap**). MP2 centrifugal distortion constants are also listed in these two tables.

Some of the CCSD results (Table 1) warrant comments. The CCSD electronic energy difference is 0.79 kJ/mol with **sc** as the *lower*-energy conformer in contrast to the MP2 predictions that **ap** is the *lower* energy conformer by 2.00 kJ/mol (see above).

The CCSD C≡P triple bond length is 154.3 pm in **ap** and 154.4 pm in **sc**, close to the corresponding equilibrium bond length of HC≡P (153.88(15) pm[63]) and the r_0 bond length of

154.4(4) pm in $CH_3C\equiv P$.[4] The C1−C3 bond length is 150.6 pm in both conformers, while C1−C2 and C2−C3 vary between 149.8 and 150.0 pm. The C−C equilibrium bond length in cyclopropane is 150.30(10) pm[64] for comparison. The lengthening of the C−C bond opposite to the substituent (C1−C3) and the shortening of the C−C bond lengths adjacent to the substituent (C1−C2 and C2−C3) is typical for substituted cyclopropanes.[65]

The bond angles of the two forms do not vary very much, however the C1−C2−C9 and C3−C2−C9 angles are about 2.5° larger in **ap** than in **sc**. A similar opening of the C2−C9−C10 bond angle of **ap** relative to **sc** is also predicted. These structural variations may indicate a slight repulsion in **ap**, or a rehybridization of the C9 carbon atom. Interestingly, the H6−C2−C9−C10 dihedral angle, which has been chosen to characterize the conformational properties of this compound, is 60.6° in **sc**, close to the "canonical" 60° and 1.7° less than the MP2 dihedral angle (see above). The fact that the CCSD dihedral angle is so close to 60° indicates that repulsive forces are not predominant.

Microwave Spectrum and Assignment of the Ground-Vibrational State Spectrum of sc. Both **ap** and **sc** have their major dipole moment components along the *a*-inertial axis according to the CCSD calculations (Table 1), with μ_a of **sc** about 15% larger than the counterpart of **ap**. Ray's asymmetry parameter[66] is −0.92 for **ap** and −0.98 for **sc**. Microwave spectra dominated by pile-ups of *a*-type *R*-branch spectral lines separated almost exactly by the sum of the rotational constants $B + C$ were expected for each rotameric form.

The CCSD method predicts that **ap** has a slightly lower electronic energy by 0.79 kJ/mol than **sc**. The latter conformer has a statistical weight of 2 relative to **ap**, whose statistical weight is 1. The lowest vibrational fundamental frequencies of the two rotamers are also similar (see Tables 1S and 2S of the Supporting Information). All this indicated that the ^aR-spectrum of **sc** should be significantly stronger than the spectrum of **ap**.

Survey spectra of CEP revealed that a strong series of pile-ups that had to belong to **sc** were the predominating feature of the spectrum. A typical example is the $J = 25 \leftarrow 24$ pile-up shown in Figure 3. The assignments of the individual K_{-1} transitions were made with ease. Several of the assignments were confirmed by RFMWDR experiments. A total of 654 ^aR-transitions were ultimately assigned for the ground vibrational state of this conformer. The maximum value of J is 44, whereas $K_{-1,max} = 27$. Searches for *b*- and *c*-type transitions were undertaken, but none were found. This is in accord with the small components of the CCSD dipole moment (0.41 and 0.01 D, respectively) along these axes (Table 1) producing insufficient intensities. The spectrum is listed in Table 5S of the Supporting Information, while the Watson *S*-reduction I^r-representation spectroscopic constants obtained in a least-squares fit using Sørensen's program Rotfit[67] are shown in Table 2. The ^aR-lines are practically independent of the quartic centrifugal distortion constants D_K, which were therefore fixed at the MP2 value in the fitting procedure. Two sextic centrifugal distortion constants, H_{JK} and H_{KJ}, had to be used in order to get a satisfactory fit.

It is interesting to compare the experimental and theoretical rotational constants. It is seen from Table 2 that the CCSD rotational constants deviate from the ground state rotational constants by 1.65%, or less. This is satisfactory because the two sets of constants are defined differently. The CCSD rotational constants are calculated from an approximate equilibrium structure, while the experimental rotational constants are

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Table 1. CCSD/cc-pVQZ Structures, Dipole Moments, and Energy Difference of the ap and sc Conformers of $C_3H_5CH_2C\equiv P$

	ap	sc		ap	sc
Bond Distance (pm)			Angle (deg)		
C1−C2	149.9	149.8	H11−C9−H12	106.7	106.7
C1−C3	150.6	150.6	C9−C10−C13	180.0	179.0
C1−H4	107.9	107.9	Dihedral Angle (deg)		
C1−H5	108.0	108.0	H4−C1−C2−H6	−1.9	−0.7
C2−C3	149.9	150.0	H4−C1−C2−C9	140.8	143.4
C2−H6	108.1	108.1	H5−C1−C2−H6	−146.9	−145.0
C2−C9	151.9	151.3	H5−C1−C2−C9	−4.2	−0.9
C3−H7	107.9	107.9	H4−C1−C3−H7	0.0	0.1
C3−H8	108.0	108.0	H4−C1−C3−H8	−144.7	−144.5
C9−C10	146.7	146.9	H5−C1−C3−H7	144.7	144.9
C9−H11	109.3	109.2	H5−C1−C3−H8	0.0	0.3
C9−H12	109.3	109.3	H6−C2−C3−H7	1.9	1.2
C10−P13	154.3	154.3	H6−C2−C3−H8	146.9	145.7
Angle (deg)			C9−C2−C3−H7	−140.8	−143.1
C2−C1−H4	117.9	118.3	C9−C2−C3−H8	4.2	1.4
C2−C1−H5	117.5	117.3	C1−C2−C9−C10	36.2	−84.2
C3−C1−H4	118.3	118.1	C1−C2−C9−H11	−85.6	153.9
C3−C1−H5	117.0	117.7	C1−C2−C9−H12	157.9	36.9
H4−C1−H5	115.1	114.7	C3−C2−C9−C10	−36.2	−154.4
C1−C2−H6	115.8	116.5	C3−C2−C9−H12	−157.9	−33.3
C1−C2−C9	121.7	119.2	H6−C2−C9−H10	180.0	60.6
C3−C2−H6	115.8	116.8	H6−C2−C9−H11	58.2	−61.3
C3−C2−C9	121.7	119.0	H6−C2−C9−N12	−58.2	−178.3
H6−C2−C9	112.4	114.5	Electronic Energy Difference (kJ/mol)		
C1−C3−H7	118.3	118.2		0.79	0.0
C1−C3−H8	117.0	117.7	Dipole Moment[a] (debye)		
C2−C3−H7	117.9	118.2	μ_a	1.18	1.41
C2−C3−H8	117.5	117.6	μ_b	0.71	0.41
H7−C3−H8	115.1	114.7	μ_c	0.0[b]	0.01
C2−C9−C10	114.7	112.5	μ_{tot}	1.38	1.47
C2−C9−H11	109.3	110.2			
C10−C9−H11	108.3	109.3			
C10−C9−H12	108.3	108.9			

[a]1 debye = 3.33564×10^{-30} C m. [b]For symmetry reasons.

Table 2. Spectroscopic Constants[a] of the Ground and Vibrational Excited States of the sc Conformer of $C_3H_5CH_2C\equiv P$

	experiment			theory
vibrational state	ground	first ex. torsion	lowest bend.	equilibrium
A_v (MHz)	9840.4(10)	9685.1(13)	9847.7(55)	10003.5
B_v (MHz)	1258.2830(25)	1260.0086(35)	1262.092(17)	1255.8
C_v (MHz)	1173.8753(26)	1175.4060(38)	1176.741(18)	1174.0
D_J (kHz)	0.37369(17)	0.37330(22)	0.38145(52)	0.387
D_{JK} (kHz)	−6.6739(22)	−6.5263(28)	−6.794(12)	−6.69
D_K (kHz)	69.1[b]	69.1[b]	69.1[b]	69.1
d_1 (kHz)	−0.06009(57)	−0.06318(83)	−0.0425(22)	−0.0640
d_2 (kHz)	−0.00196(43)	−0.02480(57)	−0.0075(13)	−0.00278
H_{JK} (Hz)	−0.01164(74)	−0.0124(10)	−0.0233(38)	−0.059
H_{KJ} (Hz)	−0.0844(29)	−0.0989(34)	−0.052(10)	0.62
rms[c]	1.250	1.345	1.488	
N[d]	654	558	203	

[a]S-reduction I^r-representation.[60] Uncertainties represent one standard deviation. The spectra are found in Tables 5S−7S of the Supporting Information. [b]Fixed at this value in the least-squares fit. [c]Root-mean-square deviation defined as $rms^2 = \Sigma[(\nu_{obs} - \nu_{calc})/u]^2/(N - P)$, where ν_{obs} and ν_{calc} are the observed and calculated frequencies, u is the uncertainty of the observed frequency, N is the number of transitions used in the least-squares fit, and P is the number of spectroscopic constants used in the fit. [d]Number of transitions used in the fit.

computed from an r_0-structure. The MP2 calculations (Table 2S; Supporting Information) predict that the equilibrium A, B, and C rotational constants should all be *smaller* by 84.8, 5.26, and 5.95 MHz, respectively. Comparison of the experimental rotational

constants of Table 2 (column 2) with the CCSD constants (last column) shows that the ground-state A rotational constant is smaller by 163.1, B is larger by 2.48, and C is smaller by 0.12 MHz. These values are different from the MP2 predictions just
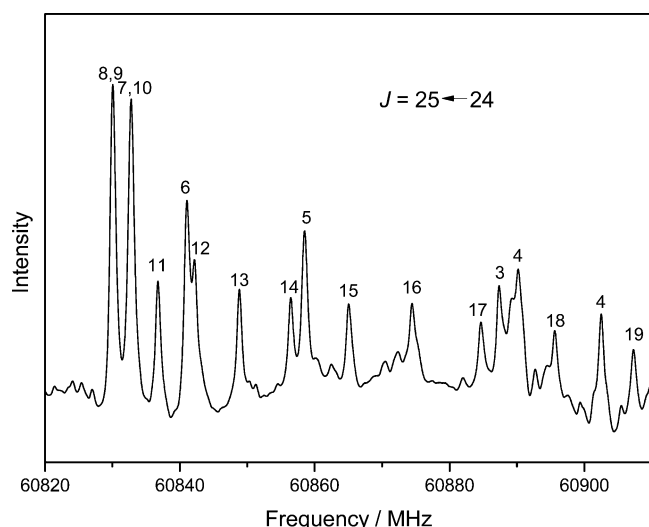
Figure 3. Portion of the $J = 25 \leftarrow 24$ a-type transitions of **sc**. The spectrum was taken at a field strength of about 1100 V/cm. Values of the K_{-1} pseudoquantum number are listed above several peaks of the ground vibrational state of **sc**. The transitions with K_{-1} quantum numbers 8 and 9 as well as 7 and 10 are not resolved. The intensity is in arbitrary units.

quoted. It is also noted that one experimental rotational constant (B) is larger than the CCSD B constant. It is unlikely that an *equilibrium* rotational constant is larger than a ground-state constant, because r_0 bond lengths are generally longer than r_e bond lengths.[61] The CCSD structure in Table 1 is undoubtedly close to the equilibrium structure, but still slightly different from the equilibrium structure. Unfortunately, computations at higher methodological levels than CCSD to obtain a structure that is even closer to the equilibrium structure are beyond our present possibilities.

The experimental quartic centrifugal distortion constants D_J, D_{JK}, and d_1 shown in Table 2 are in good agreement with their MP2 counterparts. A larger deviation is seen for d_2, but this experimental constant has a large uncertainty attached to it. The two MP2 sextic constants, H_{JK} and H_{KJ} are too inaccurate to warrant comparison with experiment, presumably because MP2/cc-pVTZ calculations are not a sufficiently high level of theory. The good agreement seen for the MP2 and experimental quartic

centrifugal distortion constants indicates that the MP2 harmonic force field is rather well reproduced in these calculations.

Vibrationally Excited States of sc. The frequencies of the lowest anharmonic vibrational fundamentals are 69, 120, 301, 319, and 344 cm^{-1} according to the MP2 calculations (Supporting Information, Table 2S). A series of transitions with similar Stark effects and RFMWDR patterns were observed. It is seen from Table 2 that the spectra of two vibrationally excited states have been assigned. A total of 558 transitions (Table 6S) were identified for the strongest excited-state spectrum, while 203 transitions (Table 7S) were assigned for the weaker spectrum. These spectra are assumed to belong to the first excited states of the lowest torsion about the C2−C9 bond and to the first excited state of the lowest bending vibration, respectively. Relative intensity measurements yielded 77(15) cm^{-1} for the torsion and 111(20) cm^{-1} for the bending vibration, compared to the MP2 values anharmonic frequencies of 69 and cm^{-1} and 120 cm^{-1}.

Vibration−rotation constants defined by $\alpha_x = X_0 - X_{ex}$[61] where X_0 is a rotational constant of the ground state and X_{ex} is a corresponding rotational constant of the excited state under consideration, are available from the entries in Table 2. The experimental vibration−rotation constants obtained from the first excited state of the torsion are $\alpha_A = 155.3(16)$, $\alpha_B = -1.7256(43)$, and $\alpha_C = -1.5370(46)$ MHz, compared to the MP2 values of 51.34, −2.01, and −1.23 MHz, respectively (Table 2S). The corresponding experimental values of the vibration−rotation constants of the lowest bending vibration are −7.3(56), −3.809(17), and −2.866(18) MHz vs the MP2 results of −71.00, −1.35, and −1.16 MHz, respectively. Unsatisfactory differences between the MP2 and experimental values are thus seen in both cases. The α's depend on the harmonic as well as the anharmonic parts of the force field. While the quartic centrifugal distortion constants indicate that the harmonic part seems to be well reproduced in the MP2 calculations, as discussed above, the poor performance in predicting accurate values for the α's and the sextic centrifugal distortion constants indicate that the MP2 method is not capable of producing a reliable anharmonic force field in the present case.

Assignment of the Ground-Vibrational State Spectrum of ap. The prediction that this rotamer has a higher CCSD energy than **sc** and a somewhat smaller μ_a dipole moment component than **sc** indicated that the ^aR-branch spectrum of **ap** should be much weaker than that of **sc**. This was also observed.

Table 3. Spectroscopic Constants$^{a,c-e}$ of the Ground and Vibrational Excited States of the ap Conformer of $C_3H_5CH_2C\equiv P$

	experiment			theory
vibrational state	ground	first ex. torsion	lowest bend.	equilibrium
A_v (MHz)	6215.36(21)	6220.04(65)	6253.73(34)	6290.4
B_v (MHz)	1654.5362(33)	1647.8215(74)	1655.1361(56)	1648.2
C_v (MHz)	1471.0434(38)	1467.7675(82)	1469.7079(63)	1469.2
$P_{cc}{}^b$ (10^{-20} u m^2)	21.601(2)	21.815(5)	21.145(4)	21.49
D_J (kHz)	0.62960(51)	0.62634(88)	0.63162(58)	0.651
D_{JK} (kHz)	−2.5697(29)	−2.2463(50)	−2.9069(39)	−2.62
D_K (kHz)	9.89$^{a,c-e}$	9.89$^{a,c-e}$	9.89$^{a,c-e}$	9.89
d_1 (kHz)	−0.1358(16)	−0.1244(34)	−0.1281(20)	−0.133
d_2 (kHz)	0.0040(11)	0.0092(22)	0.037(15)	−0.000488
rms$^{a,c-e}$	1.474	1.448	1.481	
$N^{a,c-e}$	334	129	201	

$^{a,c-e}$Comments as for Table 2. The spectra are listed in Tables 8S−10S of the Supporting Information. ^{b}Defined by $P_{cc} = (I_a + I_b - I_c)/2$, where I_a, I_b, and I_c are the principal moments of inertia. Conversion factor: $505379.05 \times 10^{-20}$ MHz u m^2.

[a]R-Branch transitions of this conformer were assigned in the same manner as described above for the spectrum of **sc**, and the assignments of several transitions were confirmed by RFMWDR tests. A total of 334 [a]R-branch lines with $J_{max} = 34$ and $K_{-1,max} = 26$, shown in Table 8S of the Supporting Information, were employed to calculate the spectroscopic constants displayed in Table 3. Only quartic centrifugal distortion constants were utilized in this case. D_K had to be fixed in the least-squares fit for a similar reason as for its **sc** counterpart.

It is seen from Table 1 that the CCSD b-component of the dipole moment of this conformer is 0.71 D, compared to 1.18 D for the a-component, while μ_c is zero for symmetry reasons. The intensity of MW spectral lines are proportional to the square of the dipole moment component, which means that the strongest b-type transitions should be roughly $^1/_3$ as intense as the strongest [a]R-lines. All three rotational constants, including the A rotational constant, are rather accurately determined (Table 3) and it should therefore be possible to predict the frequencies of the strongest b-type transitions very precisely. Extensive searches for the strongest b-type transitions of the spectrum were performed, but none were definitely assigned. It is suggested that reason for this is that the CCSD μ_b component is calculated to be too large.

The planar moment defined by $P_{cc} = (I_a + I_b - I_c)/2$, where I_a, I_b, and I_c, are the principal moments of inertia, is calculated to be $21.601(2) \times 10^{-20}$ u m^2 from the ground-state rotational constants in Table 3, nearly the same as 21.49 (same order of magnitude and units) obtained from the CCSD rotational constants. This is strong evidence that the **ap** form indeed has a symmetry plane.

The ground-state rotational constants of **ap** and the CCSD rotational constants (Table 3) are in good agreement, just as in the case of **sc**. The ground-state A rotational constant is smaller than its CCSD equivalent by 75.04 MHz, whereas the opposite is seen for the B and C rotational constants (+6.64 and +1.84 MHz, respectively). The MP2 method (Table 1S) predicts *all* three effective rotational constants to be smaller than the equilibrium constants by 33.3, 13.3, and 11.3 MHz for A, B, and C, respectively. The implication is that the CCSD structure of **ap** (Table 1) is an accurate structure, but likely to be slightly different from the equilibrium structure, just as in the case of **sc** that was discussed above.

The experimental D_J, D_{JK}, and d_1 quartic centrifugal distortion constants are in good agreement with the MP2 predictions, while d_2 is too uncertain to warrant meaningful comparison (Table 3).

Vibrationally Excited States of ap. A total of 129 transitions were assigned for a vibrationally excited state of **ap**. These transitions are listed in Table 9S of the Supporting Information, and the spectroscopic constants are repeated in Table 3. It is seen in this table that the planar moment P_{cc} increases from the ground-state value, which is typical for an out-of-symmetry plane vibration.[68] The relative intensity measurement yielded 101(20) cm^{-1} for this vibration, which is assumed to be the first excited state of the torsion about the C2−C9 bond. The MP2 anharmonic frequency of this mode is 100 cm^{-1} (Table 1S) in good agreement with the results of the relative intensity measurements just quoted. The experimental α-constants are calculated to be −4.68(68), 6.7147(81), and 3.2759(90) MHz, for α_A, α_B, and α_C, while the corresponding MP2 parameters are 1.90, 6.72, and 3.13 MHz (Table 1S).

The planar moment P_{cc} of the second excited state that was assigned, decreases upon excitation (Table 3), which is characteristic for an in-symmetry-plane bending vibration.[68] Its

vibrational frequency was found to be 108(20) cm^{-1}, while MP2 theory predicts 118 cm^{-1} (Table 1S). The experimental values of the α-constants are −38.37(40), −0.5999(65), and 1.3355(74) MHz, respectively, in relatively good agreement with the MP2 equivalents, which are −39.67, −0.90, and 1.477 MHz (Table 1S).

Internal Energy Difference. The internal energy differences between the ground vibrational state of **ap** and **sc** of CEP were determined by relative intensity measurements[69] performed on relatively strong, fully modulated absorption lines observing the precautions of Esbitt and Wilson.[70] The intensity and consequently the energy differences depend on the dipole moment component of the transitions being compared. The CCSD values of μ_a given in Table 2 were employed because experimental values are not available. The internal energy of **sc** was found to be 0.9(4) kJ/mol *lower* than the energy of **ap**. The uncertainty is an estimated one standard deviation. The experimental value is close to the CCSD energy difference of 0.79 kJ/mol (Table 2). It should be noted that the CCSD energy difference is the electronic energy difference between the approximate equilibrium structures of the two conformers, which is not exactly the same as the experimental internal energy value. The MP2 energy difference corrected for zero-point vibrational energy is 1.66 kJ/mol (see above) with **ap**, and not **sc**, as the lower-energy form, in disagreement with experiment.

CONCLUSIONS

The optimized CCSD structure of **ap** of CEP has a trivial value of 180° for the H6−C2−C9−C10 dihedral angle, whereas this angle is 60.6° in **sc**, almost identical to the "canonical" angle of exactly 60°, which is an indication that there is very little steric repulsion in **sc**.

The rotational constants of the ground vibrational state of both conformers are close to the differently defined CCSD rotational constants. MP2 calculations indicate that all rotational constants of the ground states of both rotameric forms of CEP should be smaller than the equilibrium rotational constants. Comparison of the CCSD and ground-state rotational constants of both forms shows that this is not always the case. It is therefore concluded that the CCSD structures of **ap** and **sc** are slightly different from the equilibrium structures and that calculations at even a higher level of theory are needed to obtain accurate equilibrium structures.

The MP2 method yielded quartic centrifugal distortion constants that are in fair agreement with their experimental equivalents. Larger differences between the MP2 and the experimental vibration−rotation constants (the α's) are seen, indicating the MP2 calculations are not sufficiently refined to deal accurately with these demanding computational problems.

The lower-energy conformer of CEP is **sc** by 0.9(4) kJ/mol. Similar preferences for *sc* forms have been found for the vast majority of the $C_3H_5CH_2X$ molecules, as discussed in the Introduction. The conformational behavior of $C_3H_5CH_2C\equiv P$ thus resembles that of its group 15 congener $C_3H_5CH_2C\equiv N$[43,44] and is at variance with the conformational energy properties of $C_3H_5CH_2C\equiv CH$[45] and $C_3H_5CH_2N\equiv C$.[47] The CCSD calculations predict the correct energy difference between **sc** and **ap** of CEP, whereas the MP2 calculations yield a wrong energy difference by about 2.5 kJ/mol.

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■ ASSOCIATED CONTENT

S Supporting Information

Results of the theoretical calculations, including electronic energies; molecular structures; dipole moments; harmonic and anharmonic vibrational frequencies; rotational and centrifugal distortion constants; and rotation—vibration constants. Microwave spectra of the ground and vibrationally excited states. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) Gier, T. E. HCP, a Unique Phosphorus Compound. *J. Am. Chem. Soc.* **1961**, *83*, 1769−1770.

(2) Tyler, J. K. Microwave Spectrum of Methinophosphide, CH≡P. *J. Chem. Phys.* **1964**, *40*, 1170−1171.

(3) Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C.; Westwood, N. P. C. FC≡P, C-Fluorophosphaethyne: Preparation and Detection by Photoelectron and Microwave spectroscopy. *J. Am. Chem. Soc.* **1978**, *100*, 446−448.

(4) Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. The Microwave Spectrum of 1-Phosphapropyne, CH₃C≡P. Molecular Structure, Dipole Moment, and Vibration-Rotation Analysis. *J. Mol. Spectrosc.* **1979**, *77*, 270−285.

(5) Kroto, H. W.; Nixon, J. F.; Ohno, K. The Microwave Spectrum of Phosphabutadiyne, H-C≡C-C≡P. *J. Mol. Spectrosc.* **1981**, *90*, 512−516.

(6) Cooper, T. A.; Kroto, H. W.; Nixon, J. F.; Ohashi, O. Detection of C-Cyanophosphaethyne by Microwave Spectroscopy. *J. Chem. Soc., Chem. Commun.* **1980**, 333−334.

(7) Durrant, M. C.; Kroto, H. W.; McNaughton, D.; Nixon, J. F. The New Molecule 1-Cyano-4-phosphabutadiyne, N≡C-C≡C-C≡P, Produced by Copyrolysis of Phosphorus Trichloride and 1-Cyanoprop-1-yne: Detection and Vibration-Rotation Analysis by Microwave Spectroscopy. *J. Mol. Spectrosc.* **1985**, *109*, 8−14.

(8) Ohno, K.; Kroto, H. W.; Nixon, J. F. The Microwave Spectrum of 1-Phosphabut-3-ene-1-yne, CH₂:CHC≡P. *J. Mol. Spectrosc.* **1981**, *90*, 507−511.

(9) Burckett-St. Laurent, J. C. T. R.; Cooper, T. A.; Kroto, H. W.; Nixon, J. F.; Ohashi, O.; Ohno, K. The Detection of Some Phosphaalkynes, RC≡P, Using Microwave Spectroscopy. *J. Mol. Struct.* **1982**, *79*, 215−220.

(10) Burckett-St. Laurent, J. C. T. R.; Kroto, H. W.; Nixon, J. F.; Ohno, K. The Microwave Spectrum of 1-Phenylphosphaethyne, C₆H₅C≡P. *J. Mol. Spectrosc.* **1982**, *92*, 158−161.

(11) Gaumont, A. C.; Denis, J. M. Preparation, Characterization, and Synthetic Potential of Unstable Compounds Containing Phosphorus−

Carbon Multiple Bonds. *Chem. Rev. (Washington, D. C.)* **1994**, *94*, 1413−1439.

(12) Guillemin, J. C.; Janati, T.; Denis, J. M. Lewis Base-Induced Rearrangement of Primary Ethyn-1-ylphosphines, a New and Efficient Route to Phosphaalkynes. *J. Chem. Soc., Chem. Commun.* **1992**, 415−416.

(13) Russell, C. A. New Adventures in the Molecular Chemistry of Phosphorus. *Angew. Chem., Int. Ed.* **2009**, *48*, 4895−4897.

(14) Lynam, J. M. Recent Advances in the Chemistry of Phosphaalkynes: Building Blocks for Novel Organophosphorus Compounds. *Organomet. Chem.* **2007**, *33*, 170−178.

(15) Heydt, H. The Fascinating Chemistry of 1,3,5-Triphosphinines and Valence Isomers. *Top. Curr. Chem.* **2003**, *223*, 215−249.

(16) Mack, A.; Regitz, M. Organophosphorus Compounds. Part 119. The Phosphaalkyne Cyclotetramer System. Syntheses, Valence Isomerizations, and Reactions. *Chem. Ber./Recl.* **1997**, *130*, 823−834.

(17) Regitz, M.; Hoffmann, A.; Bergstraesser, U. In *Modern Acetylene Chemistry*; Stang, P.J., Diederich, F., Eds.; VCH: Weinheim, Germany, 1995; pp 173−201.

(18) Streubel, R. Phosphaalkyne Cyclooligomers: From Dimers to Hexamers—First Steps on the Way to Phosphorus−Carbon Cage Compounds. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 436−438.

(19) Regitz, M. Organophosphorus Compounds. 75. Phosphaalkynes - New Building Blocks in Heterocyclic Chemistry. *J. Heterocycl. Chem.* **1994**, *31*, 663−677.

(20) Durig, J. R.; Yu, Z.; Zheng, C.; Guirgis, G. A. Conformational Studies of Fluoromethylcyclopropane from Temperature-Dependent FT-IR Spectra of Xenon Solutions and ab Initio Calculations. *J. Phys. Chem. A* **2004**, *108*, 5353−5364.

(21) Stølevik, R.; Bakken, P. Conformational Analysis of the Halomethyl Cyclopropanes and the Halosilyl Cyclopropanes by Molecular Mechanics Calculations. *J. Mol. Struct.* **1989**, *196*, 285−289.

(22) Saebo, S.; Kavana, K. Molecular Structure and Conformation of Fluoromethyl-Substituted Cyclopropane and Oxirane. MP4(SDQ)/6-311G** results. *J. Mol. Struct.: THEOCHEM* **1991**, *81*, 447−457.

(23) Durig, J. R.; Yu, Z.; Shen, S.; Warren, R.; Verma, V. N.; Guirgis, G. A. Conformational Studies of Monosubstituted Three-Membered Rings by Variable Temperature FT-IR Spectra of Rare Gas Solutions. *J. Mol. Struct.* **2001**, *563−564*, 141−145.

(24) Samdal, S.; Møllendal, H.; Guillemin, J.-C. Microwave Spectrum, Conformational Composition, and Dipole Moment of (Fluoromethyl)-cyclopropane (C₃H₅CH₂F). *J. Phys. Chem. A* **2014**, *118*, 2344−2352.

(25) Heineking, N.; Grabow, J. U.; Merke, I. Molecular Beam Fourier Transform Microwave Spectra of (Chloromethyl)cyclopropane and (Chloromethyl)oxirane. *J. Mol. Struct.* **2002**, *612*, 231−244.

(26) Durig, J. R.; Godbey, S. E.; Faust, S. A. Far Infrared and Low Frequency Raman Spectra and Conformational Stability of Gaseous (Chloromethyl)cyclopropane and (Bromomethyl)cyclopropane. *J. Mol. Struct.* **1988**, *176*, 123−135.

(27) Schei, S. H. (Chloromethyl)cyclopropane. Molecular Structure and Conformation in the Gas Phase as Determined by Electron Diffraction and Compared to Molecular Mechanics Calculation. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 15−23.

(28) Durig, J. R.; Shen, S.; Zhu, X.; Wurrey, C. J. Conformational and Structural Studies of Chloromethylcyclopropane and Bromomethylcyclopropane from Temperature Dependent FT-IR spectra of Xenon Solutions and Ab Initio Calculations. *J. Mol. Struct.* **1999**, *485−486*, 501−521.

(29) Wurrey, C. J.; Krishnamoorthi, R.; Pechsiri, S.; Kalasinsky, V. F. Vibrational Spectra and Conformations of (Bromomethyl)-cyclopropane and Epibromohydrin. *J. Raman Spectrosc.* **1982**, *12*, 95−101.

(30) Wurrey, C. J.; Yeh, Y. Y.; Krishnamoorthi, R.; Berry, R. J.; DeWitt, J. E.; Kalasinsky, V. F. Vibrational Spectra and Conformations of (Iodomethyl)cyclopropane and Epiiodohydrin. *J. Phys. Chem.* **1984**, *88*, 4059−4063.

(31) Newby, J. J.; Peebles, R. A.; Peebles, S. A. Heavy Atom Structure and Conformer Stabilities of Cyclopropyl Carbinol from Rotational

10000

dx.doi.org/10.1021/jp508411z | *J. Phys. Chem. A* 2014, 118, 9994−10001

Spectroscopy and Ab Initio Calculations. *J. Mol. Struct.* **2005**, *740*, 133−142.

(32) Marstokk, K.-M.; Møllendal, H. A Microwave and Ab Initio Study of the Conformational Properties and Intramolecular Hydrogen Bonding of Cyclopropanemethanethiol. *Acta Chem. Scand.* **1991**, *45*, 354−360.

(33) Cole, G. C.; Møllendal, H.; Guillemin, J.-C. Spectroscopic and Quantum Chemical Study of the Novel Compound Cyclopropylmethylselenol. *J. Phys. Chem. A* **2006**, *110*, 2134−2138.

(34) Marstokk, K. M.; Møllendal, H. Microwave spectrum,Conformational Equilibrium, Intramolecular Hydrogen Bonding, Dipole Moments, Nitrogen-14 Nuclear Quadrupole Coupling Constants and Centrifugal Distortion Constants of (Aminomethyl)cyclopropane. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 387−398.

(35) Cole, G. C.; Møllendal, H.; Guillemin, J.-C. Spectroscopic and Quantum Chemical Study of Cyclopropylmethylphosphine, a Candidate for Intramolecular Hydrogen Bonding. *J. Phys. Chem. A* **2005**, *109*, 7134−7139.

(36) Wurrey, C. J.; Shen, S.; Gounev, T. K.; Durig, J. R. Conformational Stability of Ethylcyclopropane from Raman Spectra, Temperature Dependent FT-IR Spectra of Xenon Solutions and ab Initio Calculations. *J. Mol. Struct.* **1997**, *406*, 207−218.

(37) Durig, J. R.; Little, T. S.; Zhu, X.; Dakkouri, M. Vibrational Spectra and Assignments, Conformational Stability, and ab Initio Calculations of Cyclopropylmethylsilanes. *J. Mol. Struct.* **1993**, *293*, 15−18.

(38) Foellmer, M. D.; Murray, J. M.; Serafin, M. M.; Steber, A. L.; Peebles, R. A.; Peebles, S. A.; Eichenberger, J. L.; Guirgis, G. A.; Wurrey, C. J.; Durig, J. R. Microwave Spectra and Barrier to Internal Rotation in Cyclopropylmethylsilane. *J. Phys. Chem. A* **2009**, *113*, 6077−6082.

(39) Little, T. S.; Zhu, X.; Wang, A.; Durig, J. R. Spectra and Structure of Small Ring Compounds-LXI. IR and Raman Spectra, Vibrational Assignment, Conformational Stability and Ab Initio Calculations of Cyclopropylmethylsilane. *Spectrochim. Acta, Part A* **1993**, *49A*, 1913−1933.

(40) Dakkouri, M.; Hermann, T. A Combined ab Initio and Gas-Phase Electron Diffraction Investigation of the Molecular Structure and Conformation of (Silylmethyl)cyclopropane. *J. Mol. Struct.* **1995**, *346*, 239−248.

(41) Little, T. S.; Vaughn, C. A.; Zhu, X.; Dakkouri, M.; Durig, J. R. Spectra and Structure of Small-Ring Compounds. LXII. Raman and Infrared Spectra, Conformational Stability, Vibrational Assignment and ab Initio Calculations of Cyclopropylmethyltrifluorosilane. *J. Raman Spectrosc.* **1994**, *25*, 735−746.

(42) Dakkouri, M. The Molecular Structure and Conformation of (Trifluorosilylmethyl)cyclopropane as Determined by Gas-Phase Electron Diffraction and Ab Initio Calculations. *J. Mol. Struct.* **1997**, *413−414*, 133−152.

(43) Su, C. F.; Cook, R. L.; Wurrey, C. J.; Kalasinsky, V. F. Microwave Spectrum of (Cyanomethyl) cyclopropane. *J. Mol. Spectrosc.* **1986**, *118*, 277−287.

(44) Wurrey, C. J.; Yeh, Y. Y.; Weakley, M. D.; Kalasinsky, V. F. Vibrational Spectra and Conformational Behavior of (Cyanomethyl)-cyclopropane. *J. Raman Spectrosc.* **1984**, *15*, 179−185.

(45) Caminati, W.; Danieli, R.; Dakkouri, M.; Bitschenauer, R. Conformational Equilibrium in (Cyclopropylmethyl)acetylene: A Microwave Spectroscopy and Ab Initio Calculation Study. *J. Phys. Chem.* **1995**, *99*, 1867−1872.

(46) Dakkouri, M.; Typke, V. Structural and Conformational Analysis of the Isoelectronic Isovalent Molecules: (Ethynylmethyl)cyclopropane and Ethynylcyclobutane. A Combined Electron Diffraction, Rotational Constants and ab Initio study. *J. Mol. Struct.* **2000**, *550−551*, 349−364.

(47) Samdal, S.; Møllendal, H.; Guillemin, J.-C. Microwave Spectrum, Conformational Properties, and Dipole Moment of Cyclopropylmethyl Isocyanide ($C_3H_5CH_2NC$). *J. Phys. Chem. A* **2013**, *117*, 5073−5081.

(48) Møllendal, H.; Samdal, S.; Gauss, J.; Guillemin, J.-C. Synthesis, Microwave Spectrum, Quantum Chemical Calculations, and Conformational Composition of a Novel Primary Phosphine, Cyclopropylethynylphosphine, ($C_3H_5C{\equiv}CPH_2$). *J. Phys. Chem. A* **2014**, *118*, 9419−9428.

(49) Guillemin, J. C.; Denis, J. M. Vacuum Dynamic Gas-Phase/Solid-Phase Reactions: N-Chlorination of Primary Amines and the α-Elimination of the Resulting Chloramines: Access to Reactive (E)- and (Z)-Alkanimines. *Angew. Chem.* **1982**, *94*, 715.

(50) Samdal, S.; Grønås, T.; Møllendal, H.; Guillemin, J.-C. Microwave Spectrum and Conformational Properties of 4-Isocyano-1-butene ($H_2C{=}CHCH_2CH_2N{\equiv}C$). *J. Phys. Chem. A* **2014**, *118*, 1413−14099.

(51) Wodarczyk, F. J.; Wilson, E. B., Jr. Radio Frequency-Microwave Double Resonance as a Tool in the Analysis of Microwave Spectra. *J. Mol. Spectrosc.* **1971**, *37*, 445−463.

(52) Møller, C.; Plesset, M. S. Note on the Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618−622.

(53) Cizek, J. Use of the Cluster Expansion and the Technique of Diagrams in Calculations of Correlation Effects in Atoms and Molecules. *Adv. Chem. Phys.* **1969**, *14*, 35−89.

(54) Purvis, G. D., III; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(55) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III An Efficient Reformulation of the Closed-Shell Coupled Cluster Single and Double Excitation (CCSD) Equations. *J. Chem. Phys.* **1988**, *89*, 7382−7387.

(56) Scuseria, G. E.; Schaefer, H. F., III Is Coupled Cluster Singles and Doubles (CCSD) More Computationally Intensive Than Quadratic Configuration Interaction (QCISD)? *J. Chem. Phys.* **1989**, *90*, 3700−3703.

(57) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision B.01; Gaussian, Inc: Wallingford CT, 2010.

(58) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; et al. *MOLPRO, a package of Ab Initio Programs*, .version 2010.1; University College Cardiff Consultants Limited: Cardiff, Wales, UK, 2010; http://www.molpro.net/.

(59) Peterson, K. A.; Dunning, T. H., Jr. Accurate Correlation Consistent Basis Sets for Molecular Core-Valence Correlation Effects: The Second Row Atoms Al−Ar, and the First Row Atoms B−Ne Revisited. *J. Chem. Phys.* **2002**, *117*, 10548−10560.

(60) Watson, J. K. G. *Vibrational Spectra and Structure*; Elsevier: Amsterdam, 1977; Vol. 6.

(61) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra. In Techniques of Chemistry*; John Wiley & Sons: New York, 1984; Vol. XVII., 1984.

(62) McKean, D. C.; Craig, N. C.; Law, M. M. Scaled Quantum Chemical Force Fields for 1,1-Difluorocyclopropane and the Influence of Vibrational Anharmonicity. *J. Phys. Chem. A* **2008**, *112*, 6760−6771.

(63) Puzzarini, C. An Improved Determination of the Equilibrium Structure and Molecular Properties of XBS and XCP (X = H, F, Cl) Molecules from ab Initio Calculations. *Phys. Chem. Chem. Phys.* **2004**, *6*, 344−351.

(64) Gauss, J.; Cremer, D.; Stanton, J. F. The r_e Structure of Cyclopropane. *J. Phys. Chem. A* **2000**, *104*, 1319−1324.

(65) Penn, R. E.; Boggs, J. E. Substituent-Induced Asymmetry of the Cyclopropane Ring. *J. Chem. Soc., Chem. Commun.* **1972**, 666−667.

(66) Ray, B. S. The Characteristic Values of an Asymmetric Top. *Z. Phys.* **1932**, *78*, 74−91.

(67) Sørensen, G. O. Centrifugal Distortion Analysis of Microwave Spectra of Asymmetric Top Molecules. The Microwave Spectrum of Pyridine. *J. Mol. Spectrosc.* **1967**, *22*, 325−346.

(68) Herschbach, D. R.; Laurie, V. W. Influence of Vibrations on Molecular Structure Determinations. III. Inertial Defects. *J. Chem. Phys.* **1964**, *40*, 3142−3153.

(69) Townes, C. H.; Schawlow, A. L.: *Microwave Spectroscopy*; McGraw-Hill: New York, 1955.

(70) Esbitt, A. S.; Wilson, E. B. Relative Intensity. *Rev. Sci. Instrum.* **1963**, *34*, 901−907.