Structural and Conformational Properties of 2-Propynylphosphine (Propargylphosphine) As Studied by Microwave Spectroscopy Supplemented by Quantum Chemical Calculations

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The microwave spectrum of 2-propynylphosphine (propargylphosphine), H−C≡C−CH$_2$−PH$_2$, has been investigated in the 18−26.5 and 32−48 GHz spectral regions at about −50 °C. Two conformers with different orientation of the phosphino group, denoted conformer I and conformer II, respectively, were assigned. Conformer I has a symmetry plane (C_s symmetry) with both hydrogen atoms of the phosphino group pointing toward the triple bond (C−C−P−H dihedral angles approximately 47° from syn-periplanar (0°)). The C−C−P−H dihedral angles are 73 and 167°, respectively, from syn-periplanar in conformer II. Only one of the hydrogen atoms of the phosphino group points toward the triple bond in this rotamer. Conformer I is 1.5(20) kJ/mol more stable than II. The dipole moment of II was determined to be (in units of 10^{-30} C m) $\mu_a = 0$ (assumed), $\mu_b = 3.05(7)$, $\mu_c = 1.60(9)$, and $\mu_{\text{tot}} = 3.44(9)$ [$\mu_{\text{tot}} = 1.03(3)$ D]. Two vibrationally excited states were assigned for each of the two rotamers I and II. Their frequencies were determined by relative intensity measurements. Many of the transitions of conformer II were split into two components presumably because of tunneling of the phosphino group. The tunneling frequency was determined to be 0.814(42) MHz for the ground vibrational state and 11.49(18) MHz for the first excited state of the C−P torsional vibration. Quantum chemical calculations at the B3LYP and MP2 levels of theory using the 6-311++G(3df,2pd) basis set reproduced experimental rotational constants, quartic centrifugal distortion constants, and dipole moment components within a few percent. The energy difference between the two conformers was calculated using the Gaussian-2 theory, and conformer I was found to be more stable than conformer II by 2.1 kJ/mol.

Introduction

Several 2-propynylic (propargylic) compounds, such as H−C≡C−CH$_2$OH,[1] H−C≡C−CH$_2$NH$_2$,[2] H−C≡C−CH$_2$NH(CH$_3$),[3] and H−C≡C−CH$_2$SH,[4] have been investigated by microwave (MW) spectroscopy. Only the conformer with the H−O−C−C dihedral angle +syn-clinal or −syn-clinal (IUPAC convention; some authors call this dihedral angle gauche) was found for propargyl alcohol.[1] It was alleged that the conformation with an anti-periplanar conformer does not exist as a stable rotamer in the case of propargyl alcohol.[1] The syn-clinal conformations observed for the alcohol and thiol[4] allow maximum interaction between the hydrogen (H) atom of the alcohol or thiol group on the one side and the triple bond on the other side. This interaction can be classified as weak intramolecular H bonding.

Only one conformer was again found for each of the amines H−C≡C−CH$_2$NH$_2$[2] and H−C≡C−CH$_2$NH(CH$_3$).[3] In the first of these compounds, the two H−N−C−C dihedral angles have +syn-clinal and −syn-clinal (gauche) orientation producing a symmetry plane in the molecule (C_s symmetry). The conformer identified for H−C≡C−CH$_2$NH(CH$_3$) was similar.[3] Conditions for forming intramolecular H bonds are ideal in these two amines as well.

No structural or conformational studies have been reported for propargylphosphine, H−C≡C−CH$_2$PH$_2$. This compound may exist in two different stable conformations, denoted conformer I and conformer II (see Figure 1), depending on the orientation of the phosphino group. Conformer I has C_s symmetry. The two C−C−P−H dihedral angles are ±syn-clinal (about ±50°) from the syn-periplanar (0°) conformation. One of the C−C−P−H dihedral angles in conformer II is approximately anti-periplanar (180°); the other is +syn-clinal or −syn-clinal (roughly 50°) from syn-periplanar. This conformation thus exists in two mirror image forms.

The interesting and unresolved problems presented by propargylphosphine motivated the present research. The methods we have chosen are MW spectroscopy and quantum chemical calculations. MW spectroscopy is ideal because of its high accuracy and selectivity. Quantum chemical calculations have been used to assist and supplement the experimental method.

It is of interest to compare the well-documented properties of amines with those of the corresponding phosphines. Quantum

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(1) Hirota, E. *J. Mol. Spectrosc.* **1968**, *26*, 335−350.

(2) (a) Bolton, K.; Owen, N. L.; Sheridan, J. *Nature* **1968**, *217*, 164. (b) Cervellati, R.; Caminati, W.; Degli Esposti, C.; Mirri, A. M. *J. Mol. Spectrosc.* **1977**, *66*, 389−398.

(3) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1985**, *A39*, 483−492.

(4) (a) Bolton, K.; Sheridan, J. *Spectrochim. Acta* **1970**, *26A*, 1001−1006. (b) Scappini, F.; Mäder, H.; Sheridan, J. *Z. Naturforsch.* **1973**, *28A*, 77−81. (c) Scappini, F., Favero, P. G.; Cervellati, R. *Chem. Phys. Lett.* **1975**, *33*, 499−501. (d) Mirri, A. M.; Scappini, F.; Favero, P. G. *J. Mol. Spectrosc.* **1976**, *63*, 509−520.

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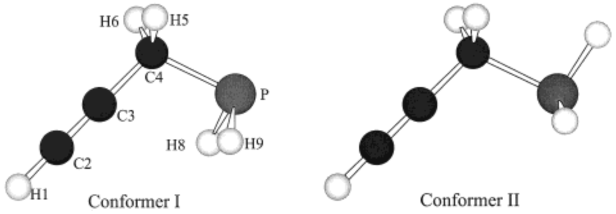

Figure 1. Two possible conformers of propargylphosphine.

chemical calculations have therefore been carried out for propargylamine.

Experimental Section

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

Two approaches for the preparation of the propargylphosphine have been reported.[5,6] We modified the second approach to prepare the propargylphosphine in gram-scale and in pure form: the vacuum line was equipped with two cells with stopcocks. The flask containing the reducing mixture (20 g of Bu_3SnH (68 mmol) with about 50 mg of duroquinone) was fitted on the vacuum line, cooled to −30 °C, and degassed. The pure 2-propynyldibromophosphine[6] (4.6 g, 20 mmol) was then slowly added with a flex-needle through the septum. This operation took about 15 min. During and after the addition, the propargylphosphine that formed was distilled off in vacuo from the reaction mixture. A cold trap (−80 °C) selectively removed the less volatile products, and the phosphine was condensed in a second cold trap (−110 °C) to remove the most volatile products (mainly PH_3). After being disconnected from the vacuum line by stopcocks, the product was kept at dry ice temperature (−78 °C) before analysis. Yield: 1.05 g, 73%.

The sample was kept at this temperature or in a refrigerator (−40 °C) when not in use. The MW spectrum was studied using the Oslo Stark spectrometer, which is described briefly in ref 7. A 3-m Stark cell made of brass was utilized. Radiofrequency microwave double-resonance (RFMWDR) experiments were carried out as described in ref 8 using the equipment mentioned in ref 9. The 18−26.5 and 32−48 GHz spectral regions were investigated with the cell cooled to about −50 °C. Lower temperatures, which would have increased the intensity of the spectrum, could not be employed owing to insufficient vapor pressure of the compound. The pressure was a few Pascals when the spectrum was recorded, and the spectrum was stored electronically using the program written by Waal.[10] The accuracy of the spectral measurements was better than ±0.10 MHz, and the maximum resolution was about 0.4 MHz. The compound was seen to react slowly even when it was kept at dry ice temperature. The reactions were more rapid during the experiments. The volatile impurity product(s), which have relatively strong MW spectra, were not identified. The contents of the cell were renewed at intervals of a few hours to minimize complications from the impurities. However, numerous absorption lines not belonging to propargylphosphine were always observed.

Results

Assignment of Conformer I. Survey spectra of propargylphosphine revealed a rich, fairly intense MW spectrum that changed somewhat each time the cell was filled with a new sample.

Table 1. Spectroscopic Constants[a,b] of Conformer I of Propargylphosphine

vibrational state	ground	first excited lowest bending	first excited C−P torsion
A/MHz	19 425.6(38)	20 743(14)	19 477(13)
B/MHz	2949.17(10)	2952.043(22)	2950.604(32)
C/MHz	2674.6161(96)	2667.183(25)	2677.468(24)
Δ_J/kHz	1.618(45)	2.17(17)	1.69(17)
$\Delta_{JK}{}^c$/kHz	−37.413(79)	−63.89(22)	−18.59(17)
$(I_A + I_B - I_C)$,[d,e] 10^{-20} u m^2	8.4257(59)	6.080(17)	8.475(19)
no. of trans in fit	34	17	16
rms[f] dev/MHz	0.087	0.169	0.132

[a] A reduction, I^r representation.[11] [b] Uncertainties represent one standard deviation. [c] Further quartic constants preset at zero; see text. [d] I_A, I_B, and I_C are the principal moments of inertia. [e] Conversion factor 505 379.05 × 10^{-20} MHz u m^2. [f] Root-mean-square deviation.

The rotational constants and components of the dipole moment along the principal inertial axes were first calculated by quantum mechanics for both rotamers. Conformer I was predicted to have a rather small dipole moment along the principal inertial a- and b-axes (B3LYP values: $\mu_a \approx 0.93$, $\mu_b \approx 0.78 \times 10^{-30}$ C m (note units)). $\mu_c = 0$ C m because this form has C_s symmetry. Moreover, conformer I was calculated to be 2.1 kJ/mol more stable than conformer II by the Gaussian-2 (G2) procedure.

It was immediately clear that conformer I could not produce the relatively intense spectrum that was observed because this rotamer has such a small dipole moment. If conformer I were to be found, its MW transitions had to be among the many weak ones that were observed.

Despite their predicted weakness, we first tried to find the ^{a}R transitions in the 32−48 GHz spectral interval using ordinary Stark spectroscopy, but there were so many candidates here that these attempts failed. The highly specific RFMWDR method[8] was then employed. This method rapidly led to unambiguous assignments of several of the ^{a}R transitions. The assignments were next gradually extended to include additional a-type R-branch lines. Their assignments were confirmed by their Stark effects and in some cases by RFMWDR experiments[8] and their fit to Watson's Hamiltonian.[11] A total of about 40 a-type transitions were ultimately assigned.

The ab initio calculations predict a small value for μ_b (ca. 0.6×10^{-30} C m). Searches for the strongest b-type transitions were made next, however, with negative results. It is assumed that the reason for this is that these transitions are indeed very weak in accord with the ab initio prediction of the dipole moment.

Conformer I is almost a prolate symmetrical top (Ray's asymmetry parameter $\kappa = -0.97$). Only two (Δ_J and Δ_{JK}) of the five Watson quartic centrifugal constants[11] were employed in the least-squares fit. The remaining quartic constants were preset at zero. The spectroscopic constants (A reduction, I^r representation[11]) are listed in Table 1. The full spectrum is listed in Table 1S in the Supporting Information.

It is seen in Table 1 that $I_A + I_B - I_C = 8.426(59) \times 10^{-20}$ u m^2 (I_A , I_B , and I_C are the principal moments of inertia). A value of 7.4 (same units) was obtained in the quantum chemical calculations below both at the B3LYP level and at the MP2 level. The close agreement is one indication that this conformation indeed has a symmetry plane with two methylene and two phosphino group out-of-plane H atoms.

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(5) Shay, R. H.; Diel, B. N.; Schubert, D. M.; Norman, A. D. *Inorg. Chem.* **1988**, *27*, 2378−2382.

(6) Guillemin, J.-C.; Malagu, K. *Organometallics* **1999**, *18*, 5259−5263.

(7) Guirgis, G. A.; Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1991**, *45*, 482−490.

(8) Wodarczyk, F. J.; Wilson, E. B. *J. Mol. Spectrosc.* **1971**, *37*, 445−463.

(9) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1988**, *A42*, 374−390.

(10) Waal, Ø. Personal communication, 1994.

(11) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1977; Vol. 6, pp 1−89.

The values of the B3LYP centrifugal distortion constants were $\Delta_J = 1.52$ and $\Delta_{JK} = -36.1$ kHz, respectively, in good agreement with the entries in Table 1. Unfortunately, it was not possible to determine the dipole moment of this conformer because the intensity of the spectrum was so low that quantitative measurements of the Stark effect could not be made.

Vibrationally Excited States of Conformer I. The RFM-WDR spectrum revealed a few vibrationally excited states of conformer I. Two of these were assigned. The spectra consisting of ^{a}R transitions are given in the Supporting Information (Tables 2S and 3S), whereas the spectroscopic constants are given in Table 1.

It is seen in this table that the rotational constants (especially the A rotational constant) change more upon excitation to the first excited state of the lowest bending vibration than to the first excited state of the C−P torsional vibration. This is expected because heavy atoms are much more involved in the former normal vibration than in the torsion.

It is also seen in Table 1 that the value of $I_A + I_B - I_C$ is considerably less for the first excited state of the lowest bending vibration ($6.080(17) \times 10^{-20}$ u m^2) than for the ground vibrational state ($8.426(59) \times 10^{-20}$ u m^2). This behavior is expected for bending vibrations having A' symmetry.[12]

The value of $I_A + I_B - I_C$ for what is assigned as the first excited state of the torsion around the C−P bond is nearly the same (see Table 1) as the corresponding value for the ground vibrational state. The rotational constants are also rather similar for the two states. This is expected because the light H atoms of the phosphino group have the largest vibrational amplitudes in the torsional motion.

Relative intensity measurements[13] yielded 161(30) cm^{-1} for the lowest bending vibration and 182(40) cm^{-1} for the lowest torsional vibration. This is in accord with the B3LYP calculations below that yield 170 and 190 cm^{-1}, respectively, for these two normal vibrations.

Assignment of Conformer II. The quantum chemical calculations below (Table 6) predict that the dipole moment of conformer II is much larger than that of conformer I (see below). The component of the dipole moment along the *b*-inertial axis is the largest one (about 3×10^{-30} C m). Conformer II was predicted to be approximately 2.1 kJ/mol less stable than conformer I at the G2 level of theory. Moreover, conformer II has a statistical weight of 2 as compared to a weight of 1 for conformer I because there are two equivalent mirror image orientations of the phosphino group in conformer II, while there is only one way to generate conformer I. The small energy difference and the relatively large dipole moment of conformer II indicated that it should be possible to find this rotamer as well. Moreover, the presence of significant amounts of conformer II would partly explain the comparatively intense MW spectrum that had at this point already been observed.

Searches for the strong b-type Q-branch transitions that were predicted from the rotational constants obtained by the theoretical calculations to occur in the 18−26.5 GHz spectral region were first made. These lines were soon found. These transitions were remarkably strong at about −50 °C, which indicates that there is indeed a small energy difference between the two forms and that this rotamer is much more polar than conformer I. Many of these ^{b}Q transitions had resolved Stark effects that confirmed the assignments.

It was now unproblematic to find the b-type R-branch transitions using the theoretical values of the rotational constants as starting points in the search procedure. A large number of transitions up to a maximum value of $J = 77$ were ultimately found. These transitions could be fitted within the expected uncertainty (about 0.1 MHz) using Watson's Hamiltonian[11] with quartic and sextic centrifugal distortion constants.

The c-type lines were then searched for because the c component of the dipole moment was predicted by the quantum calculations below to be as large as approximately 1.5×10^{-30} C m. These transitions were found with ease. Their intensities were much less than the intensities of similar b-type transitions, confirming that μ_b is significantly larger than μ_c. Finally, tentative assignments were made for several very weak absorption lines, which were assumed to be of the ^{a}R variety. This is in accord with the fact that μ_a is predicted by theory to be a tiny 0.7×10^{-30} C m.

The resolution of our spectrometer is about 0.4 MHz. It was noted that many, but not all, of the c-type lines were split (within the resolution) into two components of equal intensity. The splitting was small, typically 0.4−2 MHz. Strong b-type lines were next scrutinized for splitting, but this could not be detected. The splittings of the b-type lines must thus be less than the resolution (about 0.4 MHz).

Conformer II is not the first phosphine that displays such characteristic splittings. Similar phenomena have been observed for some of the conformers of the molecules $CH_3CH_2PH_2$,[14] $H_2PCH_2CH_2PH_2$,[15] and $H_2C{=}CHPH_2$.[16] The conformers in question all have a mirror image counterpart. The explanation offered for these observations has always been[14−16] that the splittings are caused by tunneling of the phosphino groups between two equivalent mirror image forms. This explanation is adopted for conformer II as well.

The phosphino group of this conformer performs a large-amplitude motion governed by a double-minimum potential associated with the torsion around the C−P bond. The spatial direction of the c component of the dipole moment is inverted when one conformation is transformed into its mirror image. The ground state is a symmetrical or + state denoted 0^+. The first excited state is an antisymmetrical or − state denoted 0^-. The energy separation between these two states is denoted Δ, often called the tunneling frequency. The selection rules for the a- and b-type transitions of the 0^+ and 0^- states follow rigid-rotor selection rules. The selection rules for the c-type transitions are those of a rigid rotor plus $(-) \leftarrow (+)$ or $(+) \leftarrow (-)$. In this case, deviation from rigid-rotor behavior is foreseen. A splitting of approximately 2Δ is thus expected for each c-type rotational transition.

Fortunately, a computer program has been written by Nielsen[17] to deal with spectra of this type. This program is based on the reduced Hamiltonian defined as follows:[17]

$$H_{\mathrm{red}} = |0> \{H_{\mathrm{r}}{}^{0} + H_{\mathrm{d}}{}^{0}\} < 0| + |1> \{H_{\mathrm{r}}{}^{1} + H_{\mathrm{d}}{}^{1} + W_{01}\} < 1| + |0> H_{\mathrm{c}} < 1| + |1> H_{\mathrm{c}} < 0|$$

where the label 0 corresponds to the + state and the label 1 corresponds to the − state.

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(12) Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1964**, *40*, 3142−3153.

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

(14) (a) Durig, J. R.; Cox, A. W. *J. Chem. Phys.* **1976**, *64*, 1930−1933. (b) Groner, P.; Johnson, R. D.; Durig, J. R. *J. Chem. Phys.* **1988**, *88*, 3456−3464.

(15) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1996**, *50*, 875−884.

(16) Dréan, P.; Le Guennec, M.; López, J. C.; Alonso, J. L.; Denis, J. M.; Kreglewski, M.; Demaison, J. *J. Mol. Spectrosc.* **1994**, *166*, 210−223.

(17) Nielsen, C. J. *Acta Chem Scand.* **1977**, *A 31*, 791−792.

Table 2. Spectroscopic Constants[a,b] of the 0^+ and 0^- States of the Ground Vibrational State of Conformer II of Propargylphosphine

state	0^+	0^-
A/MHz	19 547.3047(65)	19 547.2920(65)
B/MHz	3032.3404(10)	3032.3398(10)
C/MHz	2717.5677(11)	2717.5672(10)
Δ^c/MHz	0.814(42)	
Δ_J/kHz	2.1173(20)	2.1170(19)
Δ_{JK}/kHz	−47.690(33)	−47.686(33)
Δ_K/kHz	433.75(12)	433.66(12)
δ_J/kHz	0.470 50(35)	0.470 94(35)
δ_K/kHz	6.284(26)	6.244(27)
Φ_J/Hz	−0.007 58(90)	−0.007 42(88)
Φ_{JK}/Hz	−0.602(22)	−0.597(22)
Φ_{KJ}/Hz	0.0[d]	0.0[d]
Φ_K/Hz	16.15(31)	15.89(31)
ϕ_J/Hz	0.001 71(18)	0.001 79(18)
ϕ_{JK}/Hz	0.0[d]	0.0[d]
ϕ_K/Hz	0.0[d]	0.0[d]
no. of trans in fit	424	
rms[e] dev/MHz	0.135	
max value of J	77	

[a] As defined by Nielsen.[17] [b] Uncertainties represent one standard deviation. [c] $\Delta = W_{01}$ (energy separation between 0^- and 0^+ states,[17] "tunneling frequency"). [d] Preset at this value. [e] Root-mean-square deviation.

Using I^r representation[11] one has

$$H_r(v) = B^{(v)}J_b^{\,2} + C^{(v)}J_c^{\,2} + A^{(v)}J_a^{\,2}$$

where v refers to the + or the − state, respectively.

H_d = {Watson[11] quartic and sextic centrifugal distortion constants}$^{(v)}$

$$W_{01} = < 1|H_{vib}^{\ 0}|1 > - < 0|H_{vib}^{\ 0}|0 >$$

and W_{01} corresponds to Δ above.

H_c is the Coriolis term of the form

$$H_c = \mu_{ij} < J_jJ_i + J_iJ_j >$$

where i and j refer to the principal inertial axis. μ_{ij} is the reduced moment of inertia.

A large number of rotational transitions were assigned. The full ground-state spectrum of conformer II is given in Table 4S in the Supporting Information. These transitions were then fitted to this Hamiltonian. μ_{ij} was preset at zero because the splittings are so small. The rotational constants, the quartic centrifugal distortion constants, four of the sextic centrifugal distortion constants of both the 0^+ and the 0^- states, and Δ were allowed to vary freely with the results shown in Table 2.

The rotational and centrifugal distortion constants of the 0^+ and the 0^- states are practically identical, as expected. The quartic centrifugal distortion constants obtained in the B3LYP calculations below were $\Delta_J = 1.93$, $\Delta_{JK} = -44.1$, $\Delta_K = 429$, $\delta_J = 0.407$, $\delta_K = 5.75$ kHz, respectively, in good agreement with the entries in Table 2.

The tunneling frequency is rather small, just 0.814(42) MHz. The tunneling frequencies found in other phosphines are also quite small: 5.2179(66) MHz in $CH_3CH_2PH_2$,[14] 8.387(48) MHz in the anti II conformer of $H_2PCH_2CH_2PH_2$,[15] and 10.33(47) MHz in $H_2C{=}CHPH_2$.[16]

Vibrationally Excited States of Conformer II. The ^bQ transitions of the first excited state of the lowest bending vibration were assigned first. The ^bR transitions were then easy to locate. It turned out that these b-type transitions were all split by a small amount (up to about 2 MHz) into two components of equal intensity. The average frequencies of these split lines were fitted to Watson's expression[11] and used to predict the average frequencies of the c-type transitions. The c-type lines were assumed to be split by much more than their counterparts of the ground state (Table 4S) because the b-type lines are split by a larger amount than the corresponding ground-state transitions. Extensive searches were made for these rather weak c-type transitions, but they were not assigned in this dense spectrum. Ultimately, the b-type transitions of the two states denoted 1^- and 1^+ had to be used to determine the spectroscopic constants listed in Table 3. The symmetry assignments (1^- and 1^+) indicated in this table are tentative. The spectra of this excited state are found in Tables 5S and 6S in the Supporting Information.

Table 3. Spectroscopic Constants[a,b] of the 1^- and 1^+ States of the First Excited State of the Lowest Bending Vibration of Conformer II of Propargylphosphine

state[c]	1^-	1^+
A/MHz	19 759.966(18)	19 761.283(17)
B/MHz	3029.243(11)	3029.2441(67)
C/MHz	2714.612(10)	2714.5892(68)
Δ_J/kHz	2.421(40)	1.763(26)
Δ_{JK}/kHz	−47.690[d]	−47.690[d]
Δ_K/kHz	433.7[d]	433.7[d]
δ_J/kHz	0.4446(26)	0.4500(23)
δ_K/kHz	6.26[d]	6.26[d]
no. of trans in fit	25	28
rms[e] dev/MHz	0.146	0.139
max value of J	20	20

[a,b] Comments are the same as for Table 2. [c] The symmetry assignment of these states is tentative. [d] Preset at this value. [e] Root-mean-square deviation.

It is seen from Tables 2 and 3 that the rotational constants change relatively more after excitation of this mode. This is one of the reasons why this state is assumed to be the first excited state of the heavy-atom bending vibration, just as described above for the corresponding state in conformer I. Quantitative relative intensity measurements[13] were more difficult to perform for this rotamer than for conformer I because all lines were split. A value of ca. 150 cm^{-1} was found for this normal vibration.

The first excited state of the C−P torsional vibration was also assigned. Both the b- and the c-type lines were split in this case; the former ones were split by a few MHz, whereas the latter ones were split by roughly 25 MHz. The transitions were fitted to the tunneling Hamiltonian[17] just as the ground-state lines were (see above). No significant value could be obtained for the Coriolis coupling term μ_{ij}. The results are displayed in Table 4; the full spectrum is in Table 7S in the Supporting Information. It is seen in Table 4 that the tunneling frequency has increased to 11.49(18) MHz in this excited state, up from 0.814(42) MHz in the ground state (Table 2). The vibrational frequency of this state was found to be ca. 170 cm^{-1} by relative intensity measurements.[13]

Dipole Moment of Conformer II. The dipole moment of conformer II was determined from the Stark splittings of the Q-branch transitions shown in Table 5. The cell was calibrated using OCS whose dipole moment was taken to be 2.3857(68) × 10^{-30} C m.[18] It was not possible to determine an accurate value of μ_a from the Stark splittings of these transitions. This value was arbitrarily preset at 0 C m in the final fit, in agreement with the ab initio predictions. The experimental values of the components of the dipole moment along the principal inertial

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(18) Muenter, J. S. *J. Chem. Phys.* **1968**, *48*, 4544−4547.

Table 4. Spectroscopic Constants[a,b] of the 0^- and 0^+ States of the First Excited State of the C−P Torsional Vibration of Conformer II of Propargylphosphine

state[c]	1^-	1^+
A/MHz	19 515.428(46)	19 515.774(54)
B/MHz	3035.982(11)	3035.992(11)
C/MHz	2718.889(11)	2718.875(11)
Δ^c/MHz	11.49(18)	
Δ_J /kHz	2.028(77)	2.038(77)
Δ_{JK}/kHz	-43.67(18)	-45.19(20)
Δ_K/kHz	433.0[d]	433.0[d]
δ_J /kHz	0.462 75(92)	0.484 84(91)
δ_K/kHz	6.283[d]	6.283[d]
no. of trans in fit	72	
rms[e] dev/MHz	0.234	
max value of J	43	

[a−c] Comments are the same as for Table 2. [d] Preset at this value. [e] Root-mean-square deviation.

Table 5. Stark Coefficients[a] and Dipole Moments[a] of Conformer II of Propargylphosphine

		$\Delta\nu\ E^2/10^{-6}$ MHz V^{-2} cm^2	
transition	$\|M\|$	obs	calcd
$9_{1,8} \leftarrow 9_{0,9}$	9	7.22(7)	7.38
	8	6.05(7)	6.05
	7	4.85(6)	4.87
	6	3.85(5)	3.87
$8_{1,7} \leftarrow 8_{0,8}$	8	8.18(10)	7.86
$6_{1,5} \leftarrow 6_{0,6}$	6	9.25(11)	8.84
$4_{1,3} \leftarrow 4_{0,4}$	4	9.03(11)	9.41

Dipole Moment/10^{-30} C m

$\mu_a = 0.0$[b]	$\mu_b = 3.05(7)$	$\mu_c = 1.60(9)$	$\mu_{\mathrm{tot}} = 3.44(9)$

[a] Uncertainties represent one standard deviation. 1 D = 3.335 64 × 10^{-30} C m. [b] Assumed; see text.

axes agree well with the quantum chemical values calculated at the B3LYP/6-311++G(3df, 2pd) level (in 10^{-30} C m units): $\mu_c = 1.79$, $\mu_b = 3.04$, and $\mu_a = 0.68$. It is to be noted that the B3LYP method gives a much better agreement than the MP2 one (see Table 6).

Energy Difference. A rough internal energy difference between conformers I and II was determined by comparing intensities of selected transitions of the ground state of the two forms assuming Boltzmann distribution between them.[13] In addition, μ_a of conformer I was assumed to be 1.0×10^{-30} C m [0.3 D]. Conformer II was assumed to have a statistical weight of 2 relative to conformer I, whose statistical weight was assumed to be 1. An energy difference of 1.5 kJ/mol with conformer I as the most stable rotamer was obtained. The uncertainty is estimated to be as large as ±2.0 kJ/mol because only rather rough comparisons could be made in this case and because the dipole moment of conformer I is unknown. The G2 value for the energy difference is 2.2 kJ/mol with conformer I as the most stable form, as shown in the quantum chemical calculations of the next section.

Quantum Chemical Calculations. To facilitate the assignment of the microwave spectrum of a molecule such as propargylphosphine, it is useful to have at the outset of the analysis approximate values of the following parameters: (i) energy difference between the conformers; (ii) rotational constants and, if possible, quartic centrifugal distortion constants; (iii) components of the electric dipole moment; and (iv) frequencies of the lowest vibrational modes. These quantities can now easily be supplied by quantum chemical methods.[19]

Table 6. Results of Quantum Chemical Calculations for Propargylphosphine Using the 6-311++G(3df,2pd) Basis Set[a]

	conformer I		conformer II	
	B3LYP	MP2	B3LYP	MP2
$r(H_1{-}C_2)$	106.1	106.2	106.1	106.2
$r(C_2{\equiv}C_3)$	120.0	121.5	120.0	121.5
$r(C_3{-}C_4)$	144.8	145.1	145.0	145.4
$r(C_4{-}H_5)$	109.2	109.1	108.9	108.9
$r(C_4{-}H_6)$	109.2	109.1	109.2	109.1
$r(C_4{-}P)$	188.4	186.5	189.0	187.0
$r(P{-}H_8)$	141.7	140.9	142.0	141.2
$r(P{-}H_9)$	141.7	140.9	141.8	140.9
$\angle(C_3C_4H_5)$	110.57	110.52	110.48	110.37
$\angle(C_3C_4H_6)$	110.57	110.52	110.06	109.97
$\angle(H_5C_4H_6)$	106.38	106.62	107.60	108.00
$\angle(C_3C_4P)$	115.84	114.64	111.11	109.57
$\angle(C_4PH_8)$	96.92	96.36	96.01	96.43
$\angle(C_4PH_9)$	96.92	96.36	96.58	96.16
$\angle(H_8PH_9)$	93.39	93.58	93.32	93.72
$\angle C_3C_4PH_8)$	47.14	47.17	−167.02	−165.45
$\angle C_3C_4PH_9)$	−47.14	−47.17	−72.96	−70.99
$\angle(H_5PC_4H_9)$	76.25	75.81	50.21	51.43
$\angle(H_6PC_4H_8)$	−76.25	−75.81	72.98	75.08
A/MHz	20398.5	19975.3	18872.9	19416.7
B/MHz	2920.5	2974.6	2981.2	3055.4
C/MHz	2653.5	2690.1	2707.1	2735.7
μ_a /10^{-30} C m	0.93	1.28	0.68	0.77
μ_b /10^{-30} C m	0.78	0.55	3.04	3.18
μ_c /10^{-30} C m	0	0	1.78	2.14
μ_{tot} /10^{-30} C m	1.21	1.39	3.59	3.90

[a] Distances in pm, angles in deg.

All calculations for propargylphosphine were carried out with the Gaussian 94 program package.[20] To calculate an accurate energy difference between the two conformers, the G2 theory,[21] as implemented in the Gaussian 94 program, was used. Conformer I was predicted to be 2.1 kJ/mol more stable than conformer II in this way. The same calculations were repeated for propargylamine to compare the corresponding amine with propargylphosphine. A much larger difference of 6.0 kJ/mol was found in the case of the amine for its two corresponding forms.

The rotational constants, the dipole moment components, and the harmonic force field were calculated using the density-functional theory with the hybrid-functional B3LYP (Becke's three parameter functional employing the Lee, Yang, and Parr correlation functional).[22] This method was shown often to be in good agreement with experiment.[19]

The 6-311++G(3df,2pd) basis set was used. To check the reliability of the B3LYP parameters, the second-order Møller−Plesset perturbation theory (MP2)[23] was also employed. Full geometry optimization was used except for the restriction of C_s symmetry of conformer I. The results are given in Table 6.

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(19) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, PA, 1996.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(21) (a) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtis, L. A. *J. Chem. Phys.* **1989**, *90*, 5622−5629. (b) Curtis, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221−7230. (c) Curtis, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293−1298.

(22) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(23) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622.

Both methods (MP2 and B3LYP) indicate that the skeleton H−C≡C−C chain of atoms is linear within a few tenths of a degree (the maximum deviation being 0.6° for ∠(HC≡C) in conformer II). As usual, the MP2 method predicts a longer C≡C triple bond and a shorter C−P bond than B3LYP. Both procedures give angles that are in good agreement, except for the PH_2 moiety in which differences up to 2° are found. With the exception of the dihedral angles, the main difference between the structures of the two conformers is the ∠(CCP) angle, which is larger by about 5° in conformer I. A similar difference was found for the two corresponding conformers of ethylphosphine[14] and in the MP2/6-31G(d,p) structures of the appropriate conformers of 1,2-diphosphinoethane.[15]

Comparison with similar molecules shows that the C−C bond lengths in conformers I and II are very similar to the values found in CH_3CN[24] and CH_3CCH,[25] i.e., about 145−146 pm. Likewise, the C≡C triple bond lengths in conformers I and II are close to the value found in $CH_3C{\equiv}CH$,[25] i.e., 120.66(2) pm. The P−H bond lengths are not significantly different from that found in PH_3,[26] i.e., 141.3(2) pm. The predicted C−P bond lengths of the two forms vary between 189.0 and 186.5 pm (Table 6). This is slightly longer than the values determined for the corresponding two conformers of ethylphosphine (184.7 and 185.3 pm, respectively).[14]

The calculated structure is not expected to be highly accurate. The accuracy may roughly be estimated to be 0.3−0.5 pm for the bond lengths and a few tenths of a degree for the bond angles, but it could be as large as 1−3° for the dihedral angles. The deviation between the observed and the calculated values of the A rotational constants are better than 5%. The MP2 predictions are slightly more accurate than the B3LYP values. This is also the case for the B and C constants, which are predicted to be within better than 2% by either computational procedure. The theoretical quartic centrifugal distortion constants are also in fair agreement with the experimental ones. The B3LYP values for the components of the dipole moment are in very good agreement with the corresponding experimental values in the case of conformer II.

Discussion

It is interesting to compare the conformational properties of propargylphosphine with those of propargylamine. The latter molecule prefers a conformation similar to that of conformer I, as shown experimentally[2] and in the G2 calculations above (by 6.0 kJ/mol), while the title compound exists in two conformations (I and II) of almost the same energy, as shown above.

The different conformational behavior can perhaps be explained as follows: The N−H bonds are more polar than the P−H bonds. In addition, the distance between the hydrogen atoms of the amino group and the triple bond in the conformer similar to conformer I is shorter by about 0.4 Å in the amine than in the phosphine. The intramolecular hydrogen-bonding stabilization should therefore be considerably stronger in propargylamine than in the phosphine.

Moreover, the repulsion between the triple bond and the lone pair of nitrogen or phosphorus is minimal in rotamers similar to conformer I. This repulsion is likely to be larger in the amine than in the phosphine because the lone pair of the phosphorus atom is larger and more diffuse than the lone pair of nitrogen. The fact that a conformer similar to I is relatively more stable in the amine than in the phosphine is assumed to reflect a stronger repulsion between the lone pair electrons and a stronger internal hydrogen bonding in the amine than in the phosphine.

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Supporting Information Available: Tables 1S−7S contain the microwave transitions used to determine the spectroscopic constants shown in Tables 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Demaison, J.; Dubrulle, A.; Boucher, D.; Burie, J.; Typke, V. *J. Mol. Spectrosc.* **1979**, *76*, 1−16.

(25) Dubrulle, A.; Boucher, D.; Burie, J.; Demaison, J. *J. Mol. Spectrosc*. **1978**, *72*, 158−164.

(26) McRae, G. A.; Gerry, M. C. L.; Cohen, E. A. *J. Mol. Spectrosc.* **1986**, *116*, 58−70.