Structural and Conformational Properties of 4-Pentyn-1-ol As Studied by Microwave Spectroscopy and Quantum Chemical Calculations

Harald Møllendal,*,† **Helmut Dreizler,**‡ **and Dieter H. Sutter**‡

Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, Post Office Box 1033 Blindern, NO-0315 Oslo, Norway, and Institut für Physikalische Chemie, University of Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany

The microwave spectra of 4-pentyn-1-ol, $HO(CH_2)_3C \equiv CH$, and one deuterated species ($DO(CH_2)_3C \equiv CH$) have been investigated in a Stark spectrometer in the 17.5–80 GHz spectral region at about 0 °C, as well as in a pulsed-nozzle Fourier transform spectrometer in the 2.5–14 GHz range. A total of 14 spectroscopically different all-staggered rotameric forms are possible for this compound. It has previously been assumed that a conformer stabilized by intramolecular hydrogen bonding predominates in the gas phase, but the microwave spectrum of this rotamer was not assigned and it is concluded that this form is not present in high concentrations. However, the microwave spectrum indicates that several forms are present, two of which denoted **ag⁺g⁺** and **ag⁺a** were assigned in this work. In these two forms, the H−O−C−C chains of atoms have an antiperiplanar conformation and the O−C−C−C links are synclinal ("gauche"). The C−C−C−C≡CH link is synclinal in **ag⁺g⁺** but antiperiplanar in **ag⁺a**. The **ag⁺g⁺** form is determined to be 1.5(6) kJ/mol more stable than **ag⁺a** by relative intensity measurements. The microwave study was augmented by quantum chemical calculations at the MP2/6-311++G** and G3 levels of theory. Both these quantum chemical procedures indicate that there are small energy differences between several rotametric forms, in agreement with the microwave findings. Both methods predict that **ag⁺g⁺** is the global minimum.

Introduction

It has been known for a long time that π electrons of triple bonds may be involved as an acceptor group in hydrogen (H) bonding.[1] Microwave (MW) spectroscopy studies have shown that all the preferred conformers in compounds such as $HOCH_2C \equiv CH$,[2] $H_3CCH(OH)C \equiv CH$,[3] $HOCH_2C \equiv N$,[4] $H_3CCH(OH)C \equiv N$,[5] $H_2NCH_2C \equiv CH$,[6] $H_3C(NH)CH_2C \equiv CH$,[7] $H_2NCH_2C \equiv N$,[8,9] and $H_3C(NH)CH_2C \equiv N$[10] have a comparatively short contact between the hydroxyl or amine hydrogen(s) and the triple bond. This interaction may therefore be categorized as weak intramolecular H bonding, although other effects may also be of considerable importance for the conformational preferences of these compounds. The H bonds in these molecules have a ring structure formed by the five atoms of the H−X−C≡Y (X = O or N; Y = C or N) chain. This arrangement is sometimes called a "4.5-member" ring, because the H bond interaction involves the π electrons of the triple bond rather than one of the two atoms forming this bond.

The compounds $HO(CH_2)_2C \equiv CH$,[11] $HO(CH_2)_2C \equiv N$,[12] $H_2N(CH_2)_2C \equiv CH$,[13] $H_2N(CH_2)_2C \equiv N$,[14] $HS(CH_2)_2C \equiv CH$,[15] $HS(CH_2)_2C \equiv N$,[16] and $H_2P(CH_2)_2C \equiv N$[17] have an additional methylene group compared to the class of molecules mentioned above. MW studies[11–17] have shown that the preferred rotamers of these compounds are indeed stabilized by weak internal H bonds formed between the H atom of the hydroxyl, amino, thiol, or phosphino group, respectively, and the triple bond. Six atoms, H−X−C−C−C≡Y (X = O, N, S, or P; Y = C or N), form a

ring structure in these cases, but the H bonds are often called 5.5-member bonds, since the triple bond is involved rather than one of the atoms forming this bond.

There are three methylene groups in the title compound, 4-pentyn-1-ol ($HO(CH_2)_3C \equiv CH$), which was chosen for study as an extension of the these investigations. It is therefore possible for this compound to form a 6.5-member H bond involving the triple bond of the H−O−C−C−C−C≡C link of atoms. 4-Pentyn-1-ol appears to be the first example of this kind of compound studied by MW spectroscopy.

The title compound has three internal axes of rotation, namely O1−C1, C1−C2, and C2−C3 (see Figure 1). A total of 27 conformers with staggered atomic arrangements are therefore possible, but only 14 of these rotamers are spectroscopically different, because there are 13 enatiomeric pairs having identical spectra and one unique rotamer (**aaa**). Representatives of these 14 forms are sketched in Figure 1.

The H1−O1-C1−C2, O1−C1-C2−C3, and C1−C2-C3−C4 dihedral angles can be used to characterize each rotameric form. **g** is used to denote a synclinal (obsolete "gauche") dihedral angle of about 60° from synperiplanar (0°). The letter **a** stands for antiperiplanar (180° from synperiplanar); + means clockwise, and − means anticlockwise rotation about the said three bonds in the directions O1 to C1, C1 to C2, and C2 to C3.

The best conditions for intramolecular H bonding with the π electrons are found in the **g⁻g⁺g⁻** rotamer, because the distance between the H atom of the hydroxyl group and the triple bond is the shortest one of the 14 forms. The MP2/6-311++G** method predicts the distance between the midpoint of the C4−C5 triple bond and the hydrogen atom of the hydroxyl group to be 232 pm in this conformer. This is significantly shorter than the sum (290 pm) of Pauling's[18] van der Waals radii of hydrogen

* To whom correspondence should be addressed. E-mail: harald.mollendal@kjemi.uio.no.
† University of Oslo.
‡ University of Kiel.
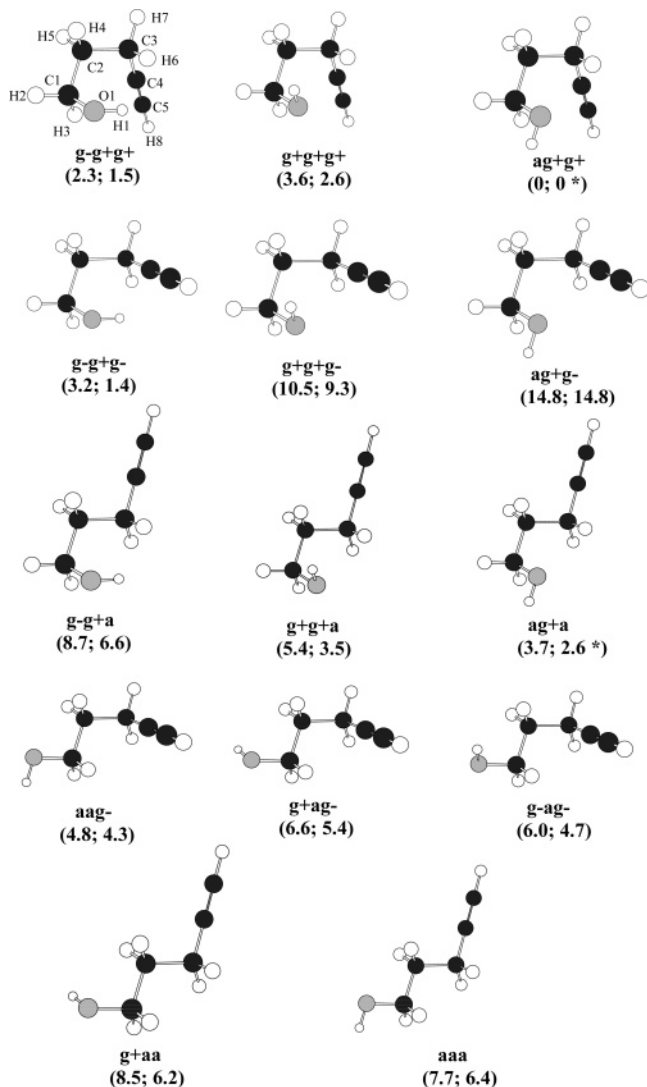
Figure 1. The 14 spectroscopically different rotamers of 4-pentyn-1-ol. Atom numbering is shown on the **g⁻g⁺g⁺** conformer. The MP2 energy difference of each rotamer (in kJ/mol) relative to **ag⁺g⁺** (0 kJ/mol) is given as the first number in the parentheses, whereas the G3 energy difference is given as the second number in the parentheses. Asterisks indicate that the spectrum of this conformer has been assigned (see text).

(120 pm) and the half-thickness of an aromatic molecule (170 pm), which is a criterion of H bonding.[1]

g⁺g⁺g⁻ is another candidate for H bonding, but conditions are much less favorable in this form than in **g⁻g⁺g⁻**, since the corresponding MP2 distance is 283 pm, only 7 pm shorter than the van der Waals sum. H-bonding is not possible in the remaining 12 rotamers because the said distance is significantly longer than 290 pm in all of them (Table 1).

An infrared spectroscopic investigation performed for a solution of 4-pentyn-1-ol in carbon tetrachloride[19] showed a relatively weak absorption band red-shifted by 50 cm⁻¹ from the major O−H stretching band. This was interpreted as evidence for the existence of rather weak intramolecular H bonding.

A combined gas-phase electron-diffraction, molecular-mechanics (MM2 method),[20] and infrared spectroscopic investigation of the gas has been reported for 4-pentyn-1-ol.[21] A red-shifted O−H stretching vibration, similar to the one observed in solution, was again seen indicating the presence of internal H bonding,[21] while the MM2 method predicted the **aaa**

conformer to be the most stable form of the molecule.[21] The electron-diffraction diagrams taken at 72 and 78 °C were interpreted as follows: The gas contains at least 50% of the H-bonded **g⁻g⁺g⁻** conformer. The **aaa** and/or the **g⁺aa** conformers also contribute substantially, while the contributions from additional rotameric forms are uncertain.[21]

The ultraviolet photoelectron spectrum has been measured and has been interpreted to indicate that intramolecular H bonding is present in 4-pentyn-1-ol.[22] Quantum chemical calculations performed recently at the MP2/6-31G(d) and MP2/6-31+G(d) levels of theory predicted that the H-bonded form, presumably **g⁻g⁺g⁻**, of the said compound is 6.6 and 3.7 kJ/mol, respectively, more stable than the second most stable rotamer, which was not specified further.[23]

Microwave (MW) spectroscopy is ideal for investigating complicated conformational equilibria because of its extremely high resolution. It is advantageous that all the 14 rotamers of 4-pentyn-1-ol each possess a sizable dipole moment (≈1.5−2.5 D), which is a prerequisite for a MW spectrum. It was decided to study its MW spectrum using two different MW spectroscopy techniques, owing to the complexity of the problem. In Oslo, Norway, static Stark-modulated spectroscopy experiments were performed, while pulsed-nozzle Fourier transform molecular beam spectrometers[24,25] were employed in Kiel, Germany. The experimental work has been augmented by quantum-chemical calculations, which were conducted with the purpose of obtaining information for use in assigning the MW spectrum and investigating properties of the Born−Oppenheimer potential-energy surface.

Experimental Section

Commercial samples were used in this work. The sample employed in Oslo, Norway, was purified by preparative gas chromatography before use. The samples utilized in Kiel were specified by the manufacturer to be more than 98% pure and were used as received. The MW spectrum was studied using the Oslo Stark spectrometer, which is described elsewhere.[26,27] The 17.5−80 GHz spectral region was investigated with the microwave absorption cell cooled to about 0 °C. A study at lower temperatures, which would have increased the intensity of the spectrum, could not be performed owing to insufficient vapor pressure of the compound. The spectra were recorded at a pressure of about 4−10 Pa and stored electronically using the computer programs by Waal[28] and Grønås.[29] The accuracy of the frequency measurements is presumed to be about 0.05 MHz, and the resolution was approximately 0.5 MHz. Microwave frequency, radio frequency double resonance (MWRFDR) experiments were performed as described by Wodarczyk and Wilson[30] employing the equipment described elsewhere.[26,27] The deuterated species, DO(CH₂)₃C≡CH, was produced by admitting fumes of D₂O into the Stark cell together with the normal species, which resulted in the production of roughly 50% deuteration of the hydroxyl group, as judged by the intensities of the MW transitions. All experiments with the deuterated species were performed in Oslo, Norway.

The experiments in Kiel were performed in the 2.5−14 GHz region with a pulsed nozzle molecular beam spectrometer with a H₀₁-resonator described elsewhere[25] and with a Fabry−Perot cavity spectrometer with a coaxial beam.[24] The low vapor pressure of the substance at room temperature prevented the preparation of a mixture of the substance with the carrier gas, He or Ar, for the supersonic expansion in the cavity. The compound was therefore exposed to a stream of the selected carrier gas in a stainless steel vessel placed in a position before the gas mixture entered the molecular beam valve.

Microwave Spectrum of 4-Pentyn-1-ol

J. Phys. Chem. A, Vol. 111, No. 46, 2007 **11803**

TABLE 1: Structures[a,b] of the 14 "Stable" Conformers of 4-Pentyn-1-ol As Calculated at the MP2/6-311++G** (Frozen Core) Level of Theory

param	g⁻g⁺g⁺	g⁺g⁺g⁺	ag⁺g⁺	g⁻g⁺g⁻	g⁺g⁺g⁻	ag⁺g⁻	g⁻g⁺a	g⁺g⁺a	ag⁺a	aag⁻	g⁺ag⁻	g⁻ag⁻	g⁺aa	aaa
						Distance (pm)								
O1−H1	96.2	96.2	**96.1**	96.3	96.2	96.1	96.1	96.2	**96.1**	96.1	96.1	96.1	96.2	96.1
C1−O1	142.6	142.7	**142.9**	142.1	142.1	142.3	142.6	142.6	**142.8**	142.7	142.4	142.5	142.4	142.6
H2−C1	109.3	109.8	**109.8**	109.3	109.9	109.9	109.2	109.8	**110.0**	110.0	109.2	109.4	109.3	109.9
H3−C1	109.7	109.2	**109.7**	110.1	109.4	110.0	110.0	109.4	**109.8**	109.7	110.0	109.7	110.0	109.9
C2−C1	152.6	152.4	**151.8**	152.8	152.6	151.9	152.4	152.4	**151.8**	151.8	152.3	152.4	152.4	151.8
H4−C2	109.5	109.8	**109.6**	109.5	109.7	109.5	109.5	109.8	**109.5**	109.5	109.5	109.5	109.5	109.4
H5−C2	109.7	109.7	**109.6**	109.7	109.7	109.7	109.6	109.6	**109.6**	109.5	109.8	109.7	109.7	109.4
C3−C2	153.8	153.7	**153.8**	153.9	154.0	154.0	153.6	153.6	**153.6**	153.7	153.8	153.7	153.6	153.6
H6−C3	109.5	109.5	**109.4**	109.6	109.6	109.6	109.8	109.7	**109.8**	109.5	109.5	109.5	109.7	109.7
H7−C3	109.5	109.6	**109.6**	109.7	109.7	109.8	109.6	109.5	**109.4**	109.7	109.7	109.7	109.7	109.7
C4−C3	146.6	146.5	**146.5**	146.7	146.6	146.5	146.3	146.4	**146.4**	146.6	146.6	146.6	146.4	146.4
C5−C4	122.1	122.0	**122.0**	122.1	122.1	122.0	122.0	122.0	**122.0**	122.0	122.0	122.0	122.0	122.0
H8−C5	106.6	106.5	**106.5**	106.6	106.5	106.5	106.5	106.5	**106.5**	106.5	106.5	106.5	106.5	106.5
H1⋯π[c]	305.6	474.0	**487.6**	232.2	282.5	407.3	529.3	498.2	**573.7**	501.7	522.2	475.7	556.2	621.0
						Angle (deg)								
H1−O1−C1	106.6	107.1	**107.5**	106.9	107.8	107.5	107.7	106.9	**107.7**	107.5	107.1	107.0	107.0	107.6
O1−C1−H2	106.1	110.8	**110.7**	105.5	111.0	111.0	105.5	110.8	**110.6**	110.7	105.7	105.5	105.5	110.8
O1−C1−H3	110.5	105.6	**110.7**	110.9	105.2	110.6	110.7	105.4	**110.8**	111.0	110.9	111.0	110.8	110.8
O1−C1−C2	112.5	112.1	**107.3**	113.3	113.7	108.6	112.9	112.5	**107.6**	107.4	112.3	112.2	112.4	107.6
C1−C2−H4	109.6	109.3	**108.9**	108.5	110.2	109.7	109.4	109.6	**109.3**	109.2	109.0	108.7	109.1	109.2
C1−C2−H5	108.4	109.0	**108.8**	108.9	107.7	107.4	108.7	109.2	**109.0**	108.6	109.3	109.6	109.6	109.2
C1−C2−C3	112.7	112.5	**112.3**	113.7	113.6	113.7	112.5	112.2	**111.8**	112.1	112.3	112.4	111.9	111.5
C2−C3−H6	109.4	109.3	**109.2**	109.6	109.4	109.0	109.4	109.3	**109.3**	109.5	109.6	109.6	108.8	108.8
C2−C3−H7	109.8	109.8	**109.6**	109.2	109.6	109.3	109.9	109.4	**109.3**	109.7	109.7	109.5	109.5	108.8
C2−C3−C4	112.5	111.8	**112.1**	113.8	112.8	114.2	112.4	112.1	**112.1**	112.6	112.3	112.4	112.1	112.2
C3−C4−C5	178.4	181.0	**180.4**	180.4	179.0	179.2	178.5	180.8	**178.0**	180.1	179.4	181.5	181.4	180.0
C4−C5−H8	179.1	179.3	**179.0**	179.9	178.5	177.9	179.6	179.4	**179.0**	179.6	179.7	179.3	179.6	179.6
						Dihedral Angle[d] (deg)								
H2−C1−O1−H1	159.6	−57.1	**64.2**	−175.2	−77.0	58.3	167.9	−60.0	**−58.5**	71.4	178.6	178.6	178.0	61.1
H3−C1−O1−H1	42.8	−173.9	**−56.6**	68.4	166.6	−61.9	51.5	176.5	**61.8**	−48.9	−64.7	62.0	−65.5	−59.1
C2−C1−O1−H1	−80.3	66.2	**183.9**	−55.3	46.7	178.4	−72.2	63.4	**178.1**	−169.0	58.4	−61.7	57.9	−179.0
H4−C2−C1−O1	−67.2	−60.6	**−60.7**	−43.6	−71.0	−61.9	−58.7	−60.3	**−60.9**	63.3	57.3	−55.0	55.3	59.0
H5−C2−C1−O1	175.1	−177.7	**−178.3**	−160.7	172.7	−178.6	−176.1	177.1	**−178.3**	−54.0	−60.1	62.3	−62.1	−58.5
C3−C2−C1−O1	53.6	60.6	**60.1**	79.2	51.6	61.4	63.0	61.3	**60.6**	−174.7	179.4	−176.3	176.9	−179.7
H6−C3−C2−C1	−70.0	−57.0	**−60.2**	179.8	159.8	158.7	53.5	61.1	**56.2**	177.8	176.9	175.9	57.2	58.7
H7−C3−C2−C1	173.3	−174.6	**−177.8**	63.0	42.6	42.5	−64.1	−55.7	**−60.6**	61.0	59.9	59.0	−59.8	−58.5
C4−C3−C2−C1	51.3	64.0	**61.0**	−58.6	−79.7	−80.3	174.8	177.6	**177.4**	−60.8	−61.7	−62.7	178.8	−179.9
H8−C5−C4−C3	178.2	−177.6	**178.1**	1.7	−174.8	163.2	−178.7	172.6	**−176.2**	172.1	161.6	164.3	178.7	−179.9

[a] Atom numbering is given in Figure 1. [b] The microwave spectra of **ag⁺g⁺** and **ag⁺a** were assigned. [c] Distance between H1 and the midpoint of the triple bond. [d] Measured from syn = 0°. Clockwise rotation corresponds to a positive dihedral angle.

The backing pressure varied from 0.5 to 1 bar. Helium was used for the lower frequencies to enlarge the Doppler splittings, while argon was employed for the higher ones. The sample interval was mostly 40 ns for 8 *k* sampling points. The averaging cycles varied from 128 to 4096, in extreme cases to 12 000 cycles. The power output of the frequency synthesizer was about 5 mW. The measuring accuracy is estimated to be ±2 kHz.

The H₀₁-resonator spectrometer[25] allows one to reach lower frequencies (down to approximately 1 GHz) with a resonator size comparable to that of the Fabry−Perot spectrometer (which has a Fresnel limit near 4 GHz). The molecular beam, coaxial to the resonator axis, first introduced by Grabow and Stahl,[31] increases the resolution and sensitivity since the interaction volume of the molecular beam and the resonator field is increased in comparison with the arrangement where the molecular beam is perpendicular to the axis of the resonator, as in the original FTMW spectrometer introduced by Balle and Flygare.[32]

Both Fourier transform microwave (FTMW) spectrometers allowed measurements of μ_b and μ_c transitions, initially not found by Stark spectroscopy, to be made. The Ritz combination principle could be used for several lines to confirm the assignments. The possibility of scanning the spectra automati-

cally proved to be very helpful. The arrangement for scans with the intrinsically fixed frequency cavity spectrometers was introduced by Andresen et al.[33] and was used extensively in this investigation.

Results and Discussion

Quantum Chemical Calculations. The quantum chemical calculations were performed by employing the Gaussian 03 suite of programs[34] running on the 64 processor HP "superdome" in Oslo, Norway. The structure, rotational constants, dipole moments, harmonic vibrational frequencies, Watson's quartic centrifugal distortion constants,[35] and energy differences were calculated for the 14 conformers shown in Figure 1. Gaussian 03 allows the calculation of anharmonic vibrational frequencies and the vibration−rotation constants (the α's),[36] but these very comprehensive calculations were calculated only for one rotamer, **ag⁺a**, because of restriction on computational resources. The 6-311++G** basis set, which is of triple-ζ quality and includes diffuse electron orbitals, was employed. Electron correlation was taken into consideration using the second-order Møller−Plesset (MP2) perturbation theory[37] with frozen-core electrons. Full geometry optimization, with no symmetry

TABLE 2: Rotational Constants, Quartic Centrifugal Distortion Constants,[a] Dipole Moments, and Energy Differences of the 14 "Stable" Conformers of 4-Pentyn-1-ol As Calculated at the MP2/6-311++G** (Frozen Core) Level of Theory[b]

param	g⁻g⁺g⁺	g⁺g⁺g⁺	ag⁺g⁺	g⁻g⁺g⁻	g⁺g⁺g⁻	ag⁺g⁻	g⁻g⁺a	g⁺g⁺a	ag⁺a	aag⁻	g⁺ag⁻	g⁻ag⁻	g⁺aa	aaa
							conformer							
							Rotational Constants (MHz)							
A	5539.3	6433.7	**6227.9**	5122.4	5622.0	5713.0	13066.2	12367.1	**12809.2**	7793.0	7615.8	7669.8	15818.9	15960.2
B	2432.8	2075.7	**2160.3**	2818.0	2576.0	2515.0	1477.5	1490.9	**1510.8**	1796.6	1803.6	1784.0	1324.0	1334.2
C	2035.0	1877.0	**1932.9**	1950.8	1937.0	1893.2	1403.3	1428.7	**1435.2**	1549.7	1549.6	1546.0	1253.6	1260.4
							Centrifugal Distortion Constants (kHz)							
Δ_J	5.95	2.34	**3.08**	2.06	2.05	2.21	0.23	0.28	**0.24**	0.82	0.84	0.82	0.14	0.14
Δ_{JK}	−21.6	−17.5	**−20.4**	−5.34	−4.04	−7.04	−2.26	−5.99	**−3.03**	−9.78	−9.93	−9.82	−9.33	−9.33
Δ_K	37.8	54.8	**55.2**	9.16	10.2	20.2	90.1	163	**108**	53.4	50.2	52.7	306	305
δ_J	1.96	0.55	**0.78**	0.77	0.64	0.78	0.022	0.004	**0.013**	0.22	0.23	0.22	0.023	0.023
δ_K	8.20	2.88	**4.01**	1.69	3.40	3.73	4.26	1.03	**3.13**	2.06	1.89	1.65	0.63	0.66
							Dipole Moment (D[c])							
μ_a	1.19	1.01	**0.64**	0.77	0.40	2.50	0.62	0.12	**1.95**	0.38	0.26	1.21	0.79	1.02
μ_b	0.76	1.86	**0.61**	2.18	1.74	0.72	0.19	1.43	**1.13**	0.70	2.15	0.45	0.23	2.00
μ_c	0.79	1.09	**1.34**	0.56	1.31	0.53	1.39	0.94	**1.08**	1.02	0.66	0.97	1.24	0.00[d]
μ_{tot}	1.61	2.38	**1.60**	2.38	2.22	2.66	1.53	1.71	**2.49**	1.29	2.27	1.62	1.49	2.24
							Energy Difference[e] (kJ/mol)							
MP2	2.3	3.6	**0.0**	3.2	10.5	14.8	8.7	5.4	**3.7**	4.8	6.6	6.0	8.5	7.7
G3	1.5	2.6	**0.0**	1.4	9.3	14.8	6.6	3.5	**2.6**	4.3	5.4	4.7	6.2	6.4

[a] *A* reduction.[35] [b] The microwave spectra of **ag⁺g⁺** and **ag⁺a** were assigned. [c] 1 D = 3.33564 × 10⁻³⁰ C m. [d] For symmetry reasons. [e] Relative to **ag⁺g⁺**, which is the global minimum in both the MP2 and G3 calculations. Total energy corrected for zero-point vibrational effects obtained in the MP2 computations: −708 005.28 kJ/mol. The G3 energy of the same conformer was −709 652.00 kJ/mol.

restrictions imposed, was made for all 14 rotamers of Figure 1 employing the default convergence criteria of Gaussian 03.

No imaginary vibrational frequencies were computed for any of the 14 forms, which is a confirmation that they are indeed minima ("stable" conformers) on the potential energy hypersurface. The geometries calculated for them are given in Table 1, which also includes the nonbonded distances between H1 and the midpoint of the triple bond, whereas Table 2 contains the rotational constants calculated from the structures in Table 1. The *A*-reduction quartic centrifugal distortion constants of Watson,[35] the principal-axis dipole moment components, and the electronic energy differences corrected for zero-point vibrational energies were calculated for the stable rotamers using the same computational procedure with the results summarized in Table 2 and shown in Figure 1 (first number in parentheses underneath each rotamer). The harmonic zero point energies vary somewhat among the conformers. The largest value (314.9 kJ/mol) is found for the hydrogen-bonded **g⁻g⁺g⁻** rotamer, and the smallest value (312.0 kJ/mol) is computed for the **aaa** conformer. This effect therefore affects the ordering of the conformational energies presented in Table 2 and Figure 1 by a maximum of 2.9 kJ/mol.

The anharmonic zero point energy of **ag⁺a** is reduced to 309.1 kJ/mol, compared to 313.1 kJ/mol calculated for the harmonic zero point energy. Similar reductions are expected for the remaining 14 conformers. It is therefore expected that anharmonicity corrections would hardly lead to a significant reordering of the relative MP2 energies from the values presented in Table 2 and Figure 1. The calculated vibration−rotation constants for this conformer are discussed below.

It is seen in this table that the MP2 energies of several of the rotamers vary by only a few kJ/mol. It was therefore decided to repeat the calculations of relative energies using the G3 method, which is renowned for calculating energy differences accurately.[38] The results of these calculations are included in the last line of Table 2 and shown as the second number in parentheses in Figure 1.

Several of the computational results warrant further comments. The MP2 bond lengths and bond angles of all the 14 forms are predicted to take their "normal" values, whereas the dihedral angles vary relatively more and deviate by as much as

about 20° from their "ideal" values (0, ±60, and ±180°) in some cases; see Table 1. These anomalies are presumably caused by intramolecular forces of various kinds.

It has been claimed[19,21−23] that the H-bonded conformer **g⁻g⁺g⁻** is the most stable form of the molecule. Interestingly, this rotamer is found to be a high-energy form relative to **ag⁺g⁺**, which is the global minimum in both in the MP2 and G3 calculations. **ag⁺g⁺**, which does not have an internal H bond, is 3.2 kJ/mol more stable than **g⁻g⁺g⁻** in MP2 and 1.4 kJ/mol more stable in the G3 calculations.

Further inspection of Table 2 reveals that five rotamers, **g⁻g⁺g⁺**, **g⁺g⁺g⁺**, **ag⁺g⁺**, **g⁻g⁺g⁻**, and **ag⁺a**, are predicted by both methods to fall within an energy range of less than 4 kJ/mol, which is within the uncertainty limit of these calculations. The energies of **g⁺g⁺a**, **aag⁻**, **g⁺ag⁻**, **g⁻ag⁻**, and **aaa** are predicted to be 3.5−7.7 kJ/mol less stable than the global minimum (**ag⁺g⁺**). The conclusion is therefore that the quantum chemical calculations indicate that the gaseous state of 4-pentyn-1-ol consists of a mixture of several rotamers present in significant concentrations and it is quite uncertain which conformer represents the global energy minimum.

MW Spectrum and Assignment of the Ground Vibrational State of ag⁺a. The Stark MW spectrum of 4-pentyn-1-ol taken at about 0 °C is comparatively weak and very crowded with absorption lines occurring every few MHz throughout the entire frequency range, which indicates that several rotamers may be present.

Survey spectra taken by the Oslo spectrometer using a relatively low Stark field strength of about 100 V/cm revealed the characteristic pile-ups of transitions belonging to a prolate rotor with a large dipole moment along the *a*-inertial axis. These pile-ups were separated by roughly 2.9 GHz. Inspection of Table 2 reveals that this spectrum had to belong to either **g⁻g⁺a**, **g⁺g⁺a**, or **ag⁺a**, with **ag⁺a** as most likely candidate because this conformer has a much larger μ_a than the other two alternatives. Using the MWRFDR technique,[30] several a-type R-branch transitions with $K_{-1} = 3$ were soon assigned. This was the key to the assignment of the ᵃR-branch spectrum. The preliminary spectroscopic constants obtained in Oslo, Norway, were used to predict the frequencies of low-*J* b- and c-type lines, which were subsequently identified employing the pulsed-nozzle

Microwave Spectrum of 4-Pentyn-1-ol

J. Phys. Chem. A, Vol. 111, No. 46, 2007 **11805**

TABLE 3: Spectroscopic Constants^a of the Ground Vibrational State of the ag$^+$a Conformer of HO(CH$_2$)$_3$C≡CH and DO(CH$_2$)$_3$C≡CH

param	species		
	parent^b	deuterated^b	predicted^c
A (MHz)	12723.2440(17)	12521.0(33)	12809.2
B (MHz)	1507.699 00(26)	1463.9219(41)	1510.8
C (MHz)	1435.555 30(28)	1393.4126(46)	1435.2
Δ_J (kHz)	0.259 15(46)	0.2565(54)	0.24
Δ_{JK} (kHz)	−4.1472(21)	−4.16(7)	−3.03
Δ_K (kHz)	126.0(5)	126.0^d	108
δ_J (kHz)	0.014 630(77)	0.014 630^d	0.013
δ_K (kHz)	1.928(26)	1.928^d	3.13
rms^e	2.1129	2.9257	
no. of transitions^f	226	39	

^{a} A reduction I^r representation.[35] Uncertainties represent one standard deviation. ^{b} The spectra are listed in the Supporting Information, Table 1S and 6S, respectively. ^{c} MP2 predictions for the parent species; see text. ^{d} Fixed. ^{e} Root-mean-square deviation. ^{f} Number of transitions used in the least-squares fit.

Fourier transform spectrometer in Kiel, Germany. The high-J ^{b}Q-lines up to $J = 42$ were then assigned in the Stark spectrum. No c-type lines could be assigned unambiguously in the Stark spectrum, presumably because μ_c is too small, producing insufficient intensities for these transitions. The full spectrum consisting of 226 transitions is listed in the Supporting Information, Table 1S. The spectroscopic constants (*A*-reduction, I^r representation)[35] are shown in Table 3 together with the spectroscopic constants calculated for the **ag$^+$a** rotamer for convenient comparison with their experimental counterparts. The rotational and the five quartic centrifugal distortion constant were fitted using Sørensen's program ROTFIT.[39] Inclusion of Watson's sextic centrifugal distortion constants[35] resulted in insignificant improvement of the least-squares fit and were therefore not employed in the final fit shown in Table 1S. The inverse squares of the estimated uncertainties of 0.002 (Fourier transform spectrosocpy) and 0.05 MHz (Stark spectroscopy) were used as weights in the fitting procedure.

Comparison of the experimental spectroscopic constants (Table 3) with the MP2 counterparts (Tables 1 and 3) shows that there is very good agreement (better than 1%) between the theoretical and experimental rotational constants for the **ag$^+$a** rotamer. The quartic centrifugal distortion constants are also in good agreement. The dipole moment could not be determined by Stark spectroscopy owing to the low intensities of the low-J transitions, which are normally employed for this purpose. The prediction of a predominating μ_a (Table 2) and significantly smaller μ_b and μ_c for this conformer is also in agreement with the MW observations.

Vibrationally Excited States of ag$^+$a. The ground-state transitions in the Stark spectrum were accompanied by series of transitions presumably belonging to vibrationally excited states of **ag$^+$a**. The ^{a}R-branch transitions of three such excited states belonging to two different normal modes of vibration were assigned. No b- or c-type lines were found presumably because they are too weak. The spectroscopic constants of these excited states are listed in Table 4, whereas the spectra are found in the Supporting Information, Tables S2−S4. The excited states are assumed to be the first and second excited state of the torsion about the C2−C3 bond and the first excited state of the lowest bending vibration.

The vibration−rotation constants can be calculated from the entries in Tables 3 and 4 using the formula $\alpha_X = X_0 - X_1$,[36] where X_0 comprises the rotational constants *A*, *B*, or *C* of the ground vibrational state (Table 3) and X_1 comprises the

corresponding rotational constants of the excited state under consideration. The experimental values are (from Tables 3 and 4) $\alpha_A = 211.5$ MHz, $\alpha_B = -2.76$ MHz, and $\alpha_C = -3.31$ MHz for the torsional vibration, compared to the MP2 values 217.7, −2.15, and −3.61 MHz, respectively. Relative intensity measurements yielded 65(20) cm^{-1} for this vibration. The uncorrected harmonic and anharmonic values calculated for the torsion are the same, 68 cm^{-1}. The experimental rotation−vibration constants for the bending vibration are −257(15), 0.90, and 2.84 MHz, respectively, compared to MP2 result of −206.9, 0.48, and 0.75 MHz. The first excited state of the lowest bending vibration was found to be 123(30) cm^{-1} by relative intensity measurements, whereas the uncorrected MP2 value for this normal mode is 133 cm^{-1}, compared to 131 cm^{-1}, which is found when anharmonicity is taken into account in the calculations.

Deuterated Species of ag$^+$a. The assignment of the ^{a}R-transitions of the ground vibrational state of the **ag$^+$a** species of DO(CH$_2$)$_3$C≡CH was straightforward. The spectrum is shown in Table 5S in the Supporting Information, and the spectroscopic constants are listed in Table 3. Only two quartic centrifugal distortion (Δ_J and (Δ_{JK}) constants were fitted in this case, while the three remaining constants ((Δ_K, δ_J, and δ_K) were preset at the values of the parent species.

It is now possible to calculate the principal-axes ("substitution") coordinates[40] of the hydrogen atom of the hydroxyl group from the rotational constants of the parent and deuterated species using Kraitchman's equations.[41] The substitution coordinates of this hydrogen atom obtained in this manner are $|a| = 317.0(1)$, $|b| = 81.1(3)$, and $|c| = 9.9(29)$ pm, where the uncertainties have been calculated by propagating the uncertainties of the rotational constants. The Costain uncertainties[42] of these coordinates using the *K*-value of hydrogen as recommended by van Eijck[43] are almost the same (0.1, 0.4, and 31 pm for $|a|$, $|b|$, $|c|$, respectively). The MP2 values for these coordinates are 319, 80, and 6 pm, respectively, in good agreement with the substitution coordinates. This constitutes independent evidence that the spectra of the **ag$^+$a** conformer (Tables 1S−5S) have indeed been assigned and not confused with the spectra of any of the other 13 rotatmers, which are possible for this compound.

MW Spectrum and Assignment of the Ground Vibrational State of ag$^+$g$^+$. This rotamer is predicted to be the global energy minimum both in the MP2 as well as in the G3 calculations. Searches for this conformer using the Fourier transform spectrometer in Kiel lead to the successful assignment of its MW spectrum. Low-J a-, b-, and c-type lines were measured using this technique. The c-type lines were much stronger than a- and b-type transitions. The transitions assigned in this manner were used to predict the frequencies of lines involving higher values of the J quantum number. Searches for them were then made employing the Stark MW spectrometer in Oslo, Norway, which resulted in the assignment of many additional c-type lines. No definite assignments could be made for a- and b-type transitions using this technique, presumably because they have too low intensities to allow unambiguous assignments to be made. These observations are in accord with μ_c being much larger than both μ_a and μ_b. The calculated values of 0.64, 0.61, and 1.34 D, respectively, of the three dipole moment components (Table 2) are in agreement with these findings.

A total of 431 transitions with a maximum value of $J = 60$ were ultimately assigned and used to determine the spectroscopic constants shown in Table 5, while the full spectrum is found in Table 6S in the Supporting Information. Centrifugal distortion is prominent in this conformer as values up to ≈6.5 GHz were

TABLE 4: Spectroscopic Constants^a of Vibrationally Excited States of the ag$^+$a Conformer of HO(CH$_2$)$_3$C≡CH

	vibrational state		
param	1st excited C2−C3 torsion^b	2nd excited C2−C3 torsion^c	1st excited lowest bending^d
A (MHz)	12511.7(40)	12220(8)	12980(15)
B (MHz)	1510.4585(34)	1512.4586(55)	1506.797(11)
C (MHz)	1438.8658(28)	1441.6317(55)	1432.713(10)
Δ_J (kHz)	0.2776(24)	0.2416(2)	0.2668
Δ_{JK} (kHz)	−4.702(9)	−1.66(8)	−6.437(35)
Δ_K (kHz)	126.0^e	126.0^e	126.0^e
δ_J (kHz)	0.0146 30^e	0.0146 30^e	0.0146 30^e
δ_K (kHz)	1.928^e	1.928^e	1.928^e
rms^f	2.6123	2.4032	2.1845
no. of transitions^g	66	49	29

^{a} A reduction I^r representation.[35] Uncertainties represent one standard deviation. ^{b} The spectrum is listed in the Supporting Information, Table 2S. ^{c} Table 3S. ^{d} Table 4S. ^{e} Fixed. ^{f} Root-mean-square deviation. ^{g} Number of transitions used in the least-squares fit.

TABLE 5: Spectroscopic Constants^a of the Ground Vibrational State of the ag$^+$g$^+$ Conformer of HO(CH$_2$)$_3$C≡CH and DO(CH$_2$)$_3$C≡CH

	species		
param	parent^b	deuterated^b	predicted^c
A (MHz)	6469.511 64(56)	6287.3293(75)	6227.9
B (MHz)	2082.944 27(22)	2032.922(22)	2160.3
C (MHz)	1885.279 05(21)	1832.632(30)	1932.9
Δ_J (kHz)	2.917 45(35)	2.91745^d	3.08
Δ_{JK} (kHz)	−23.2800(31)	−22.602(33)	−20.4
Δ_K (kHz)	72.5809(91)	69.06(14)	55.2
δ_J (kHz)	0.729 96(13)	0.664(11)	0.780
δ_K (kHz)	5.208(17)	5.208^d	4.01
Φ_J (Hz)	0.02116(20)	0.0^d	
Φ_{JK} (Hz)	0.0^d	0.0^d	
Φ_{KJ} (Hz)	−0.773(18)	0.0^d	
Φ_K (Hz)	2.135(53)	0.0^d	
ϕ_J (Hz)	0.008 207(55)	0.0^d	
ϕ_{JK} (Hz)	0.0873(78)	0.0^d	
ϕ_K (Hz)	3.089(52)	0.0^d	
rms^e	1.9981	2.0397	
no. of transitions^f	431	62	

^{a} A reduction I^r representation.[35] Uncertainties represent one standard deviation. ^{b} The spectra are listed in the Supporting Information, Tables 6S and 7S, respectively. ^{c} MP2 predictions for the parent species. The sextic centrifugal distortion constants were not predicted; see text. ^{d} Fixed. ^{e} Root-mean-square deviation. ^{f} Number of transitions used in the least-squares fit.

found (Table 6S), and this made it possible to determine six of the seven sextic centrifugal distortion constants (Table 5) in addition to the five quartic constants. The only sextic constants that could not be determined was Φ_{JK}, which was assigned a value of zero in the final least-squares fit, which is reported in Table 6S. The MP2 rotational and quartic centrifugal distortion constants of this rotamer have also been included in Table 5 for convenient comparison with experiment. Searches for the spectra of vibrationally excited states of this rotamer were made using Stark spectroscopy but met with no success, presumably because they are too weak.

Deuterated Species of ag$^+$g$^+$ and Conformer Assignment. Comparison of the experimental rotational constants in Table 5 of the parent species of **ag$^+$g$^+$** with the MP2 rotational constants (Tables 2 and 5) reveals differences of about 3.7% in the cases of A and B and 2.4% in the case of C. The agreement with the MP2 rotational constants of **g$^+$g$^+$g$^+$** is even better, in fact less than 1% in each case. A distinction between **ag$^+$g$^+$** and **g$^+$g$^+$g$^+$** cannot therefore be made only by comparison of the rotational constants. Additional evidence is required for a safe conformer assignment.

The rotational constants of the deuterated species (DO-(CH$_2$)$_3$C≡CH) can be used to distinguish between the two

alternatives. The assignment of the MW spectrum of this species was straightforward; the spectroscopic constants are displayed in Table 5, and the spectrum is listed in Table 7S. The substitution coordinates of the hydrogen atom of the hydroxyl group calculated in the same manner as above from the entries in Table 5 are $|a| = 237.9(1)$, $|b| = 143.4(1)$, and $|c| = 54.5(3)$ pm, where the uncertainties have been obtained by propagation of the standard deviations of the rotational constants. The Costain uncertainties[42,43] are in this case 0.1, 0.2, and 0.6 pm for $|a|$, $|b|$, and $|c|$, respectively. The corresponding values of the MP2 structure of **ag$^+$g$^+$** are 221, 154, and 43 pm, respectively, whereas the corresponding MP2 values of **g$^+$g$^+$g$^+$** are 260, 14, and 78 pm, respectively. The agreement between the substitution and MP2 coordinates of this hydrogen atom is therefore much better in the case of **ag$^+$g$^+$** than in the case of **g$^+$g$^+$g$^+$**.

Additional evidence is the fact that the μ_c lines are much stronger than the μ_b transitions, which indicates that μ_c is significantly larger than μ_b. This is predicted (Table 2) for **ag$^+$g$^+$**, whereas the opposite is predicted for **g$^+$g$^+$g$^+$**.

Interestingly, the MP2 centrifugal distortion constants of **ag$^+$g$^+$** (Tables 2 and 5) are in better agreement with the experimental values (Table 5) than the centrifugal distortion constants of **g$^+$g$^+$g$^+$** (Table 2) are, which is an additional, however weak, indication that **ag$^+$g$^+$** has been identified and not confused with **g$^+$g$^+$g$^+$**. The theoretical predictions (Table 2) that **ag$^+$g$^+$** is the global minimum also supports the present conformer assignment.

Searches for Further Conformers. Extensive searches for the MW spectra of additional conformers were performed using both Fourier transform and Stark spectroscopies. While thermodynamic equilibrium exists in the static Stark experiment, this is not the case for the Fourier transform experiment, which is an additional complication with this molecular beam method. The quantum chemical predictions in Table 2 guided these attempts to assign additional rotameric forms. The efforts to find the spectra of unidentified conformers predicted (Table 2) to have the lowest energies (i.e. **g$^-$g$^+$g$^+$**, **g$^+$g$^+$g$^+$**, **g$^-$g$^+$g$^-$**, and **aag$^-$**) were more extensive than the searches for the high-energy rotamers (**g$^+$g$^+$g$^-$**, **ag$^+$g$^-$**, **g$^-$g$^+$a**, **g$^+$g$^+$a**, **g$^+$ag$^-$**, **g$^-$ag$^-$**, **g$^+$aa**, and **aaa**). The most comprehensive searches were made in an attempt to assign the spectrum of the H-bonded rotamer **g$^-$g$^+$g$^-$**, because it has been claimed that a large fraction of the gas is this form.[21]

The investigations using Fourier transform spectroscopy were aimed at predicted frequencies from the rotational constants in Table 2 of comparatively strong low-J transitions of specific rotamers rather than scanning the full 2.5−14 GHz range. The frequency range to be scanned for a given transition was

Microwave Spectrum of 4-Pentyn-1-ol

J. Phys. Chem. A, Vol. 111, No. 46, 2007 **11807**

estimated from the assumed uncertainties of the MP2 rotational constants. The ranges were at least ±30 MHz about the predicted frequency of a selected transition but considerably more in most cases. The spectrum of the **ag⁺g⁺** conformer was successfully assigned in this manner.

The Fourier transform spectrum also revealed several unidentified transitions in addition to those that were assigned for **ag⁺g⁺** and **ag⁺a**. These unidentified transitions were in many cases used to predict frequencies or frequency ranges for additional transitions of the MW spectrum of the conformer under consideration. These predicted frequencies or frequency ranges were then scanned in an attempt to assign the spectrum. For example, the hypothetical rotamer **g⁺g⁺g⁺** is predicted to have $\mu_a \approx 1$ D and to be 3.6 (MP2) or 2.6 kJ/mol (G3) less stable than **ag⁺g⁺** (Table 2). The a-type $1_{0,1} - 0_{0,0}$ transition of this conformer has a frequency $\nu = B + C$, where B and C are the rotational constants. This frequency is predicted to occur in the vicinity of 3952.7 MHz, according to the rotational constants given in Table 2. A scan from 3920 to 4067 MHz revealed a line at 3992.5 MHz. However, the line corresponding to the $3_{2,2} - 2_{2,1}$ transition with a frequency of $\nu = 3B + 3C$ could not be detected, even with 4098 averaging cycles. Many similar attempts to assign the spectra of additional rotameric forms were made in vain.

Several relatively strong lines observed in the Fourier transform experiment could not be assigned. For example, a complete scan of the 3.5−4.15 GHz range revealed six such transitions. It is therefore possible that at a very extensive scan of the total range of the spectrometer (2.5−14 GHz) would be useful for the assignment of further conformers.

A fairly large number of comparatively strong transitions in the Stark spectrum remained unassigned after the assignments of the spectra of the two rotamers above had been completed. These unassigned lines could belong to the spectra of additional conformers, or they could belong to vibrationally excited states of both assigned and unassigned conformers. The Stark modulation patterns of these transitions were investigated in an attempt to assign them. The selective and efficient MWRFDR technique[30] was also employed for the same purpose in those cases where this method is most useful (ᵃR-transitions of prolate rotors), but these extensive efforts met with no success.

It is concluded that we cannot see how the spectrum of a large fraction (≈50%) of the H-bonded **g⁻g⁺g⁻**, as alleged in the electron-diffraction investigation,[21] with a μ_b as large as ≈ 2.2 D (Table 2) could have avoided being assigned. The coexistence of rotamers other than the two assigned here (**ag⁺g⁺** and **ag⁺a**), including a minor fraction of **g⁻g⁺g⁻** as well as other of the 14 rotameric forms, seems, however, to be likely.

Energy Difference. The internal energy difference between conformers **ag⁺a** and **ag⁺g⁺** has been derived using a variant of eq 3 of Esbitt and Wilson.[44] According to Wilson,[45] the internal energy difference is given by

$$E_v - E'_{v'} = E'_{J'} - E_J + RT \ln L \qquad (1)$$

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 investigation, R is the universal gas constant, and T is the absolute temperature. L is given by

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

where S is the peak signal amplitude of the radiation-unsaturated line, g is the degeneracy other than the rotational degeneracy, which is $2J + 1$. ν is the frequency of the transition, μ is the principal-axis dipole moment component, l is the radiation wavelength in the Stark cell,[46] $\Delta\nu$ 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 **ag⁺a** and **ag⁺g⁺** was determined by comparing the intensities of $K_{-1} = 11$, 12, and 13 lines of the a-type $23 \leftarrow 22$ transition of **ag⁺a** at ≈67.7 GHz with the $J = 13$, 14, and 15 of the $K_{-1} = 8 \leftarrow 7$ c-type Q-branch series at ≈67.2 GHz. These lines were selected because they have very rapid Stark effects and are comparatively strong. The intensity comparison was made using a relatively low Stark field strength of about 45 V/cm. Modulation of unwanted interfering lines was avoided in this manner. The statistical weights (g) were assumed to be the same (2) for both rotamers. The dipole moment components of the two forms were those predicted in the MP2 calculations (Table 2).

The internal energy difference of the ground vibrational states, $E\mathbf{ag^+a} - E\mathbf{ag^+g^+}$ obtained this in way varied between +1.0 and +2.2 kJ/mol (**ag⁺g⁺** *more* stable than **ag⁺a**). The average value was found to be $E\mathbf{ag^+a} - E\mathbf{ag^+g^+} = 1.5$ kJ/mol. There are several sources of errors in this procedure. One standard deviation has been estimated to be ±0.6 kJ/mol by evaluating the uncertainties associated with the many parameters of eq 2.

The experimental finding that **ag⁺g⁺** is more stable than **ag⁺a** by 1.5(6) kJ/mol compares well with the MP2 prediction (3.7 kJ/mol) and the G3 result (2.6 kJ/mol), as seen from Table 2.

Conclusions

The conformer composition of the gas phase of 4-pentyn-1-ol, HO(CH₂)₃C≡CH, has been investigated by Stark modulated and MW Fourier transform spectroscopy and quantum chemical calculations at the MP2/6-311++G** and G3 levels of theory. A total of 14 conformers that are spectroscopically different may exist for this compound. The microwave spectra of the parent and one deurerated species of the title compound strongly indicate that several rotamers of this compound are present in relatively high concentrations. The MW spectra of two conformers, **ag⁺a** and **ag⁺g⁺**, have been assigned and **ag⁺g⁺** has been determined to be *more* stable than **ag⁺a** by 1.5(6) kJ/mol by relative intensity measurements. Extensive, but unsuccessful, searches were made in the MW spectrum for additional rotameric forms.

It has previously been claimed[21] that the conformational mixture is dominated by the H-bonded conformer **g⁻g⁺g⁻**, but the MW spectrum does not support this view. This form is likely to be present but in a relatively small concentration.

The MP2 and G3 calculations predict that several rotameric forms are separated by energy differences of only a few kJ/mol. The assigned rotamer **ag⁺g⁺** is predicted to be the global minimum, and the H-bonded conformer **g⁻g⁺g⁻** is calculated to be a high-energy form in both theoretical procedures, which is in agreement with the present experimental observations.

Supporting Information Available: Microwave spectra of the parent and deuterated species of 4-pentyn-1-ol. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: New York, 1960.

(2) Hirota, E. *J. Mol. Spectrosc.* **1968**, *26*, 335.

(3) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1985**, *39*, 639.

(4) Cazzoli, G.; Lister, D. G.; Mirri, A. M. *J. Chem. Soc.*, *Faraday Trans. 2* **1973**, *69*, 569.

(5) Caminati, W.; Meyer, R.; Oldani, M.; Scappini, F. *J. Chem. Phys.* **1985**, *83*, 3729.

(6) Cervellati, R.; Caminati, W.; Degli Esposti, C.; Mirri, A. M. *J. Mol. Spectrosc.* **1977**, *66*, 389.

(7) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1985**, *39*, 483.

(8) Pickett, H. M. *J. Mol. Spectrosc.* **1973**, *46*, 335.

(9) Macdonald, J. N.; Tyler, J. K. *J. Chem. Soc., Chem. Commun.* **1972**, 995.

(10) Braathen, O.-A.; Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1985**, *39*, 605.

(11) Szalanski, L. B.; Ford, R. G. *J. Mol. Spectrosc.* **1975**, *54*, 148.

(12) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1985**, *39*, 15.

(13) Braathen, O.-A.; Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1985**, *39*, 209.

(14) Braathen, O.-A.; Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1983**, *37*, 493.

(15) Cole, G. C.; Møllendal, H.; Guillemin, J.-C. *J. Phys. Chem. A* **2006**, *110*, 9370.

(16) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1983**, *37*, 477.

(17) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1983**, *37*, 755.

(18) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(19) Schleyer, P. v. R.; Trifan, D. S.; Bacskai, R. *J. Am. Chem. Soc.* **1958**, *80*, 6691.

(20) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(21) Trætteberg, M.; Bakken, P.; Seip, R.; Lüttke, W.; Knieriem, B. *Acta Chem. Scand., Ser. A* **1988**, *42*, 584.

(22) Kowski, K.; Lüttke, W.; Rademacher, P. *J. Mol. Struct.* **2001**, *231*, 567−568.

(23) Vélez, E.; Quijano, J.; Gaviria, J.; Roux, M. V.; Jiménez, P.; Temprado, M.; Martín-Valcárcel, G.; Pérez-Parajón, J.; Notario, R. *J. Phys. Chem. A* **2005**, *109*, 7832.

(24) Grabow, J.-U.; Stahl, W.; Dreizler, H. *Rev. Sci. Instrum.* **1996**, *67*, 4072.

(25) Storm, V.; Dreizler, H.; Consalvo, D.; Grabow, J.-U.; Merke, I. *Rev. Sci. Instrum.* **1996**, *67*, 2714.

(26) Møllendal, H.; Leonov, A.; de Meijere, A. *J. Phys. Chem. A* **2005**, *109*, 6344.

(27) Møllendal, H.; Cole, G. C.; Guillemin, J.-C. *J. Phys. Chem. A* **2006**, *110*, 921.

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

(29) Grønås, T. Personal communication, 2003.

(30) Wodarczyk, F. J.; Wilson, E. B., Jr. *J. Mol. Spectrosc.* **1971**, *37*, 445.

(31) Grabow, J. U.; Stahl, W. *Z. Naturforsch. A* **1990**, *45*, 1043.

(32) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33.

(33) Andresen, U.; Dreizler, H.; Grabow, J. U.; Stahl, W. *Rev. Sci. Instrum.* **1990**, *61*, 3694.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

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

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

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

(38) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(39) Sørensen, G. O. ROTFIT. Personal communication, 1972.

(40) Costain, C. C. *J. Chem. Phys.* **1958**, *29*, 864.

(41) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17.

(42) Costain, C. C. *Trans. Am. Crystallogr. Assoc.* **1966**, *2*, 157.

(43) Van Eijck, B. P. *J. Mol. Spectrosc.* **1982**, *91*, 348.

(44) Esbitt, A. S.; Wilson, E. B. *Rev. Sci. Instrum.* **1963**, *34*, 901.

(45) Wilson, E. B. Personal communication.

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