Microwave Spectrum of 3-Butyne-1-thiol: Evidence for Intramolecular S−H···π Hydrogen Bonding

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The microwave spectrum of 3-butyne-1-thiol has been studied by means of Stark-modulation microwave spectroscopy and quantum-chemical calculations employing the B3LYP/6-311++G(3df,2pd), MP2/aug-cc-pVTZ, MP2/6-311++G(3df,2pd), and G3 methods. Rotational transitions attributable to two conformers of this molecule were assigned. One of these conformers possesses an antiperiplanar arrangement of the atoms S−C1−C2−C3, while the other is synclinal and stabilized by the formation of an intramolecular hydrogen bond between the H-atom of the thiol group and the π-electrons of the C≡C triple bond. The energy difference between these conformers was estimated to be 1.7(4) kJ mol^{-1} by relative intensity measurements, with the hydrogen-bonded conformer being lower in energy. The spectra of five vibrationally excited states of the synclinal conformer were observed, and an assignment of these states to particular vibrational modes was made with the aid of a density functional theory (DFT) calculation of the vibrational frequencies at the B3LYP/6-311++G(3df,2pd) level of theory.

Introduction

Despite the comparatively small difference in electronegativity between sulfur and hydrogen (2.58 vs 2.20),[1] the ability of thiol groups to act as hydrogen bond donors to suitable acceptor groups has been known since the 1960s.[2,3] The formation of hydrogen bonds by thiol groups is of some importance in biological systems, where hydrogen bonding by the −SH group of cysteine to O and N atoms, and even to aromatic rings, influences the structure and activity of protein molecules.[4] However, the number of molecules containing the thiol functional group that have been studied by microwave spectroscopy remains small, despite the suitability of this form of spectroscopy for the investigation of intramolecular hydrogen bonding.

Of the thiols studied to date, of which cyclopropanemethanethiol ($C_3H_5CH_2SH$),[5] 2-furanmethanethiol ($C_4H_3OCH_2SH$),[6] 3-mercaptopropionitrile ($HSCH_2CH_2CN$),[7] 1,2-ethanedithiol ($HSCH_2CH_2SH$),[8] allyl mercaptan ($H_2C{=}CHCH_2SH$),[9] and 3-butene-1-thiol ($HSCH_2CH_2CH{=}CH_2$)[10,11] are examples, a propensity is shown for the formation of intramolecular hydrogen bonds, when suitable acceptor groups are present. The subject of the present investigation also allows a comparison to be made with the structurally similar molecules 3-butyne-1-ol ($HC{\equiv}CCH_2CH_2OH$),[12] 3-butyne-1-amine ($HC{\equiv}CCH_2CH_2NH_2$),[13] and 3-mercaptopropionitrile ($HSCH_2CH_2CN$),[7] all of which are stabilized by intramolecular hydrogen bonding involving π electrons of triple bonds in their lowest-energy conformers.

Experimental Section

Caution: Low molecular weight thiols are often powerfully malodorous. All reactions and handling should be carried out in a well-ventilated hood.

Microwave Experiment. The spectrum of 3-butyne-1-thiol was recorded in the 12.4−80.0 GHz frequency interval by Stark-modulation microwave spectroscopy, using the microwave spectrometer at the University of Oslo, which measures the frequency of individual transitions with an estimated accuracy of ∼0.1 MHz. Details of the construction and operation of this device have been given elsewhere.[14] While recording the spectrum, the Stark cell was cooled to approximately −10 °C with solid CO_2, in an attempt to increase the intensity of the spectrum.

Radio frequency microwave double-resonance experiments (RFMWDR), similar to those performed by Wodarczyk and Wilson,[15] were also conducted to assign unambiguously particular rotational transitions.

Preparation of 3-Butyne-1-thiol. The synthesis of 3-butyne-1-thiol has already been reported. It was prepared by treating 4-bromobut-1-yne with thiourea, followed by reduction of the formed product[16] or by reaction of ethanethioic acid S-3-butynyl ester with potassium carbonate.[17] By analogy with the approach we reported to prepare various unsaturated selenols,[18,19] we synthesized 3-butyne-1-thiol by reduction of the corresponding thiocyanate with lithium aluminum hydride followed by acidification of the formed thiolate using a vacuum line.

Synthesis of Thiocyanic Acid, 3-Butyne Ester. In a 100 mL two-necked flask equipped with a stirring bar and a nitrogen inlet were introduced the 3-butyne-1-ol, methanesulfonate (2.96 g, 20 mmol),[20] dry acetonitrile (30 mL), and potassium thiocyanate (2.06 g, 21 mmol). After 3 h of stirring at 70 °C, the solution was cooled at room temperature, precipitated potassium bromide was filtered off, and the solvent was removed in vacuo. The thiocyanate was purified by distillation in vacuo and obtained in 87% yield (1.93 g, 17.4 mmol). Bp: 39 °C (0.5 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.16 (t, 1H, $^4J_{HH}$ = 2.7 Hz, CH), 2.77 (td, 2H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 2.7 Hz, $CH_2C{\equiv}C$), 3.12 (t, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2S). ^{13}C NMR

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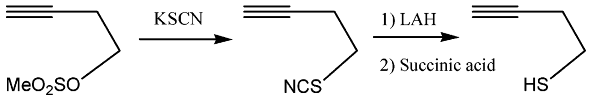
SCHEME 1



($CDCl_3$, 100 MHz, δ): 19.8 (t, $^1J_{CH} = 134.1$ Hz, $CH_2C{\equiv}C$), 32.3 (d, $^1J_{CH} = 146.6$ Hz, CH_2S), 71.3 (d, $^1J_{CH} = 250.5$ Hz, $C{\equiv}CH$), 79.3 (d, $^2J_{CH} = 49.8$ Hz, $C{\equiv}CH$), 111.2 (s, CN). HRMS calcd for C_5H_5NS: 111.0143; found: 111.014. IR (ν, cm^{-1}): 3293 (s, $\nu C{\equiv}CH$), 2914 (m), 2252 (w, $\nu C{\equiv}C$), 2156 (s, ν_{CN}), 1423 (s), 1290 (s), 1234 (s), 973 (m), 901 (m), 647 (s, ν_{CS}).

3-Butyne-1-thiol. The apparatus previously described for the reduction of dibromopropargylphosphine was used.[21] A 100-mL two-necked flask equipped with a septum and containing a suspension of succinic acid (3.56 g, 30 mmol) in tetraglyme (20 mL) was attached to a vacuum line, immersed in a bath cooled to 0 °C, and degassed. In a 25-mL two-necked flask equipped with a stirring bar and a nitrogen inlet, lithium aluminum hydride (200 mg, 5.2 mmol) and tetraglyme (10 mL) were introduced. The flask was immersed in a bath cooled to 0 °C, and the thiocyanic acid, 3-butyne ester (444 mg, 4 mmol) diluted in tetraglyme (3 mL), was slowly added. After 10 min of stirring, this solution was slowly added (15 min) with a syringe through the septum into the flask containing the succinic acid. During and after the addition, 3-butyne-1-thiol was distilled off in a vacuum (10^{-1} mbar) from the reaction mixture. A first cold trap (-30 °C) selectively removed the less volatile products, and 3-butyne-1-thiol was selectively condensed in a second trap cooled to -70 °C. At the end of the reaction, this second trap was disconnected from the vacuum line by stopcocks and attached to the microwave spectrometer. Yield: 90%. Bp ≈ -40 °C (0.1 mmHg). ^1H NMR (400, MHz, $CDCl_3$, δ): 1.73 (t, 1H, $^3J_{HH} = 7.8$ Hz, SH), 2.08 (t, 1H, $^4J_{HH} = 2.6$ Hz, CH), 2.52 (td, 2H, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 2.6$ Hz, $CH_2C{\equiv}C$), 2.70 (td, 2H, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 6.6$ Hz, CH_2S). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 23.3 (t, $^1J_{CH} = 143.7$ Hz, CH_2S), 23.4 (d, $^1J_{CH} = 133.3$ Hz, $CH_2C{\equiv}C$), 69.9 (d, $^1J_{CH} = 249.0$ Hz, $C{\equiv}CH$), 81.7 (d, $^2J_{CH} = 49.8$ Hz, $C{\equiv}CH$).

The deuterated compound, 3-butyne-1-thiol-*d* ($HC{\equiv}CCH_2CH_2SD$), was generated in situ, by admitting a small volume of D_2O vapor from above a liquid sample at room temperature into the cavity of the spectrometer, which already contained a few pascal of 3-butyne-1-thiol vapor. Exchange of a single D atom with the H atom of the thiol group occurred readily, resulting in an estimated 50% deuteration.

Results

Quantum-Chemical Calculations. A series of quantum-chemical calculations were conducted on 3-butyne-1-thiol, with the purpose of obtaining information for use in assigning the microwave spectrum and investigating the structures of the five conformers associated with minima on the potential-energy surface of this molecule. All calculations were performed using the Gaussian 03 suite of programs,[22] running on a 64 processor HP "superdome" computer.[23]

Geometry optimizations were carried out on the five possible conformers of 3-butyne-1-thiol, which are shown in Figure 1. Optimized geometries were obtained from self-consistent field calculations, in which the effects of electron correlation were included by the use of second-order Møller−Plesset perturbation theory (MP2),[24] as well as density functional theory (DFT) methods. MP2 optimizations were undertaken using both the 6-311++G(3df,2pd) basis set[25,26] and Dunning's extensive aug-cc-pVTZ basis,[27] which includes polarized functions for valence electrons and is augmented by additional diffuse functions. DFT optimizations were performed using the B3LYP hybrid functional (Becke's three-parameter hybrid functional,[28] employing the Lee, Yang, and Parr correlational functional[29]) in conjunction with the 6-311++G(3df,2pd) basis set. The predicted equilibrium rotational constants from these calculations are given in Table 1, and the estimates of the relative energies of the five conformers of 3-butyne-1-thiol are given in Table 2. The structure obtained for conformer V at the MP2/aug-cc-pVTZ level of theory is discussed further in a later section, while the structures obtained for the remaining four conformers are included in the Supporting Information, Table 10S.

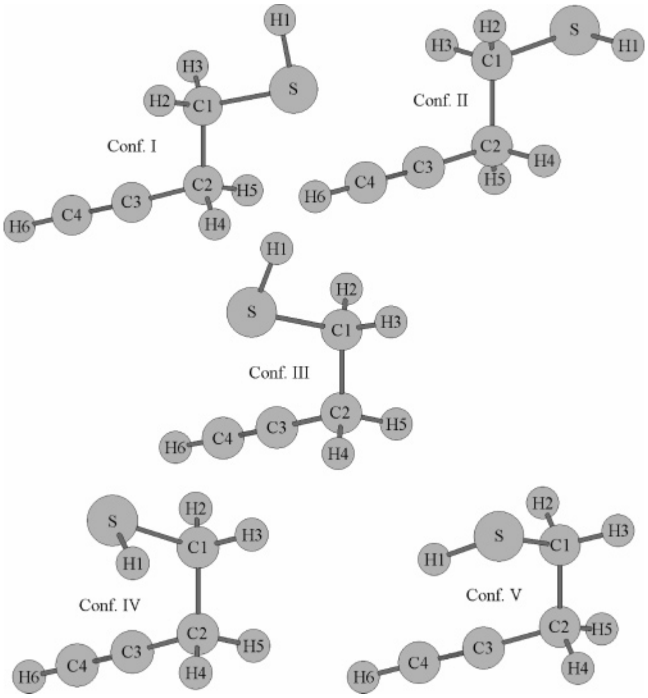


Figure 1. Structures of the five possible conformers of 3-butyne-1-thiol predicted by ab initio geometry optimizations carried out with the Gaussian 03 electronic structure package. The MP2/aug-cc-pVTZ level of theory was employed.

The B3LYP/6-311++G(3df,2pd) level of theory was also used to calculate the quartic centrifugal distortion constants for the various conformers, as these calculations are rather computationally demanding and would, therefore, take a long time to perform at the MP2/aug-cc-pVTZ level. These parameters were used with the approximate equilibrium rotational constants from geometry optimizations at the MP2/aug-cc-pVTZ level, to enable a prediction of the ground-state rotational spectra of the five conformers of 3-butyne-1-thiol to be made.

Additionally, the relative energies of the conformers were calculated using the G3 method,[30] which is tailored to the calculation of energy differences. The results of these calculations are included in Table 2.

Assignment of Conformer V. The calculated relative energies of the five conformers suggest, with the exception of the B3LYP/6-311++G(3df,2pd) estimates, that conformer V will be the lowest in energy by 2−3 kJ mol^{-1}. Therefore, our assignment of the microwave spectrum of 3-butyne-1-thiol began with this conformer.

A calculation of the dipole-moment components of 3-butyne-1-thiol, conformer V, at the B3LYP/6-311++G(3df,2pd) level of theory yielded the values $\mu_a = 0.91$ D, $\mu_b = 1.06$ D, and $\mu_c = 0.43$ D. Since a-type, R-branch rotational transitions can often

TABLE 1: Comparison of the Spectroscopic Constants[a] Obtained for Two Conformers of 3-Butyne-1-thiol, from Quantum-chemical Calculations and Experiment

	conformer II			conformer V		
spectroscopic constant	B3LYP/6-311++ (3df,2pd)	MP2/aug-cc-pVTZ	experiment	B3LYP/6-311++ (3df,2pd)	MP2/aug-cc-pVTZ	experiment
A/MHz	24706.8309	24309.5367	24309.5367[b]	7873.8043	7477.9628	7621.0796(27)
B/MHz	1471.1994	1490.5510	1497.30(52)	2258.4268	2424.8083	2359.0982(6)
C/MHz	1423.9224	1440.3422	1420.96(52)	1868.2765	1955.1672	1920.1111(6)
Δ_J/kHz	0.147973		0.1860(16)	2.061640		2.0599(4)
Δ_{JK}/kHz	−6.658237		−7.068(9)	−17.202453		−15.341(3)
Δ_K/kHz	302.578597		302.578597[c]	54.910928		44.667(9)
δ_J/kHz	0.011357		0.011357[c]	0.622865		0.64045(15)
δ_K/kHz	0.533544		0.533544[c]	4.050558		3.715(6)

[a] Uncertainties represent one standard deviation. [b] This parameter is fixed at the value obtained from a geometry optimization at the MP2/aug-cc-pVTZ level of theory. [c] Fixed at the value obtained from a DFT calculation at the B3LYP/6-311++G(3df,2pd) level of theory.

TABLE 2: Comparison of the Relative Energies[a] of Five Conformers of 3-Butyne-1-thiol, Obtained from Ab Initio Calculations and Experiment

	conformer				
method	I	II	III	IV	V
B3LYP/6-311++G(3df,2pd)	+3.98	0.00	+8.43	+5.55	+0.66
MP2/6-311++G(3df,2pd)	+6.53	+2.63	+8.64	+6.17	0.00
MP2/aug-cc-pVTZ	+6.50	+2.96	+8.79	+6.61	0.00
G3	+5.68	+2.02	+7.99	+5.42	0.00

[a] Relative energies are given in kJ mol^{-1}.

be distinguished by the characteristic patterns they form, these were the first transitions to be sought, using the prediction described above. The accuracy of this prediction was, however, somewhat lower than expected; the $J = 15 \leftarrow 14$ transitions were eventually found over 1 GHz from their predicted frequencies. Fortunately, the spacings between the high-K_{-1}, ${}^{a}R$ transitions were reproduced with a sufficient accuracy to allow their identification. Once a number of rotational transitions had been assigned, they were subjected to a least-squares analysis using Sørensen's Rotfit program.[31] By use of this preliminary fit, further a-type transitions were identified, and eventually, the frequencies of b-type and c-type transitions could be accurately predicted and assigned. The rotational constants and centrifugal distortion constants (A-reduction I^r representation[32]) obtained from the least-squares fit are given in Table 3, while the transition frequencies and residual errors are given in the Supporting Information, Table 3S. It was found that the sextic centrifugal distortion constants Φ_{JK} and φ_J were required, in addition to the five quartic centrifugal distortion constants, to give a satisfactory fit.

Once the ground-state spectroscopic constants of this conformer were precisely determined, radio frequency microwave double-resonance (RFMWDR) experiments were used to identify rotational transitions belonging to the vibrationally excited states of the molecule. Specifically, this technique allows selected pairs of *a*-type, R-branch transitions with the same value of K_{-1} to be observed, while suppressing other lines in the microwave spectrum, allowing the pair of ground-state transitions, and often several vibrational satellites, to be measured without being obscured by other spectral lines. This is of use in the assignment of excited-state spectra, which can have a low intensity in comparison with the ground-state spectrum. By use of this method, the rotational spectra of five vibrationally excited species corresponding to conformer V, labeled V*a*1, V*a*2, V*b*1, V*b*2, and V*ab*1, were assigned. The rotational constants and centrifugal distortion constants obtained from the least-squares analysis of these transitions can be found in Table 4, while the rotational transition frequencies and residuals are presented in Tables 5S−9S. A tentative assignment of these spectra to specific vibrational modes has been made, with assistance from a DFT calculation of the vibrational frequencies of this conformer at the B3LYP/6-311++G(3df,2pd) level of theory. To this end, the excited-state spectra V*a*1 and V*a*2 were attributed to the first and second excitations of the lowest-bending vibration, whereas V*b*1 and V*b*2 were assigned to the first and second excitations of the torsional motion about the C1−C2 bond, while the state V*ab*1 involved a single excitation of both of these vibrational modes. Figure 2 features a section of spectrum showing a number of transitions belonging to conformer V and gives an indication of the density of transitions in the a-type, R-branch "pile-ups", as well as typical signal-to-noise ratios.

Relative intensity measurements of the type employed by Esbitt and Wilson[33] were used to evaluate the difference in energy between the ground state and the first excited states of these two vibrational modes. The first excited state of the torsional motion about the C1−C2 bond was predicted to be 95 cm^{-1} above the ground state, according to the B3LYP/6-311++G(3df,2pd) calculation, while the value obtained from relative intensity measurements was 106 cm^{-1}. Meanwhile, the first excited state of the lowest-bending vibration was predicted by DFT calculation to be 184 cm^{-1} above the ground state, whereas the corresponding experimental value is 217 cm^{-1}. Since the error associated with the values obtained from relative intensity measurements is estimated to be of the order of ±20 cm^{-1}, this represents a reasonable agreement between theoretical and experimental values.

Assignment of Conformer II. Since the spectrum of the lowest-energy conformer of 3-butyne-1-thiol had been assigned, an attempt was made to identify transitions belonging to the conformer predicted to be second lowest in energy, namely, conformer II. The geometry optimization performed for this conformer at the MP2/aug-cc-pVTZ level of theory predicted that the components of the dipole moment along the principal inertial axes would be $\mu_a = 0.72$ D, $\mu_b = 0.06$ D, and $\mu_c = 0.65$ D. Attempts to assign the spectrum of this conformer concentrated once more on the a-type, R-branch transitions, which were identified by use of the prediction described in the section on Quantum-Chemical Calculations. The least-squares fit of these transitions gave the rotational constants and centrifugal distortion constants given in Table 3, while the rotational transition frequencies and residuals are presented in the Supporting Information in Table 1S.

The comparatively large error associated with the A rotational constant can be attributed to the fact that only a-type, R-branch transitions having a value of $K_a \geq 7$ were assigned. The absence of low-K_a lines is not unexpected, since these transitions are

TABLE 3: Experimental Spectroscopic Constants[a] for Two Conformers of 3-Butyne-1-thiol

	conformer II		conformer V	
spectroscopic constant	parent species	deuterated	parent species	deuterated
A/MHz	24309.5367[b]	22521.5215[b]	7621.0796(27)	7386.120(24)
B/MHz	1497.30(52)	1449.27(55)	2359.0982(6)	2356.1440(32)
C/MHz	1420.96(52)	1425.30(56)	1920.1111(6)	1903.4404(33)
Δ_J/kHz	0.1860(16)	0.141(3)	2.0599(4)	2.090(5)
Δ_{JK}/kHz	−7.068(9)	−6.115(7)	−15.341(3)	−14.312(11)
Δ_K/kHz	302.578597[c]	302.578597[c]	44.667(9)	44.667[d]
δ_J/kHz	0.011357[c]	0.011357[c]	0.64045(15)	0.6440(8)
δ_K/kHz	0.533544[c]	0.533544[c]	3.715(6)	3.419(20)
Φ_{JK}/Hz			0.0222(9)	
ϕ_J/Hz			0.000515(23)	
σ/kHz	0.17	0.08	0.20	0.15
N^c	193	60	522	101

[a] A-reduction I^r representation.[32] Uncertainties represent one standard deviation. [b] Fixed at the value obtained from a geometry optimization at the MP2/aug-cc-pVTZ level of theory. [c] Constant fixed at the value obtained from a density functional theory calculation at the B3LYP/6-311++(3df,2pd) level of theory. [d] Fixed at the value obtained for the parent isotopomer of this conformer.

TABLE 4: Experimental Spectroscopic Constants[a] for Six Vibrational States of Conformer V of 3-Butyne-1-thiol

	vibrational state					
spectroscopic constant	ground state	V*a*1	V*a*2	V*b*1	V*b*2	V*ab*1
A/MHz	7621.0796(27)	7617.42(20)	7621.0796[b]	7621.0796[b]	7621.0796[b]	7621.0796[b]
B/MHz	2359.0982(6)	2360.2360(40)	2361.224(22)	2345.163(51)	2332.25(35)	2346.32(20)
C/MHz	1920.1111(6)	1921.0045(39)	1921.572(27)	1914.578(63)	1908.50(47)	1915.26(28)
Δ_J/kHz	2.0599(4)	2.073(5)	2.0599[b]	2.027(9)	2.0599[b]	2.0599[b]
Δ_{JK}/kHz	−15.341(3)	−15.326(16)	−15.341[b]	−15.66(5)	−15.341[b]	−15.341[b]
Δ_K/kHz	44.667(9)	44.667[b]	44.667[b]	44.667[b]	44.667[b]	44.667[b]
δ_J/kHz	0.64045(15)	0.64045[b]	0.64045[b]	0.64045[b]	0.64045[b]	0.64045[b]
δ_K/kHz	3.715(6)	3.715[b]	3.715[b]	3.715[b]	3.715[b]	3.715[b]
σ/kHz	0.20	0.19	0.18	0.17	0.46	0.28
N^c	522	101	46	68	10	10

[a] Comments same as those for Table 3. [b] Fixed at the value obtained for the vibrational ground state of this conformer.

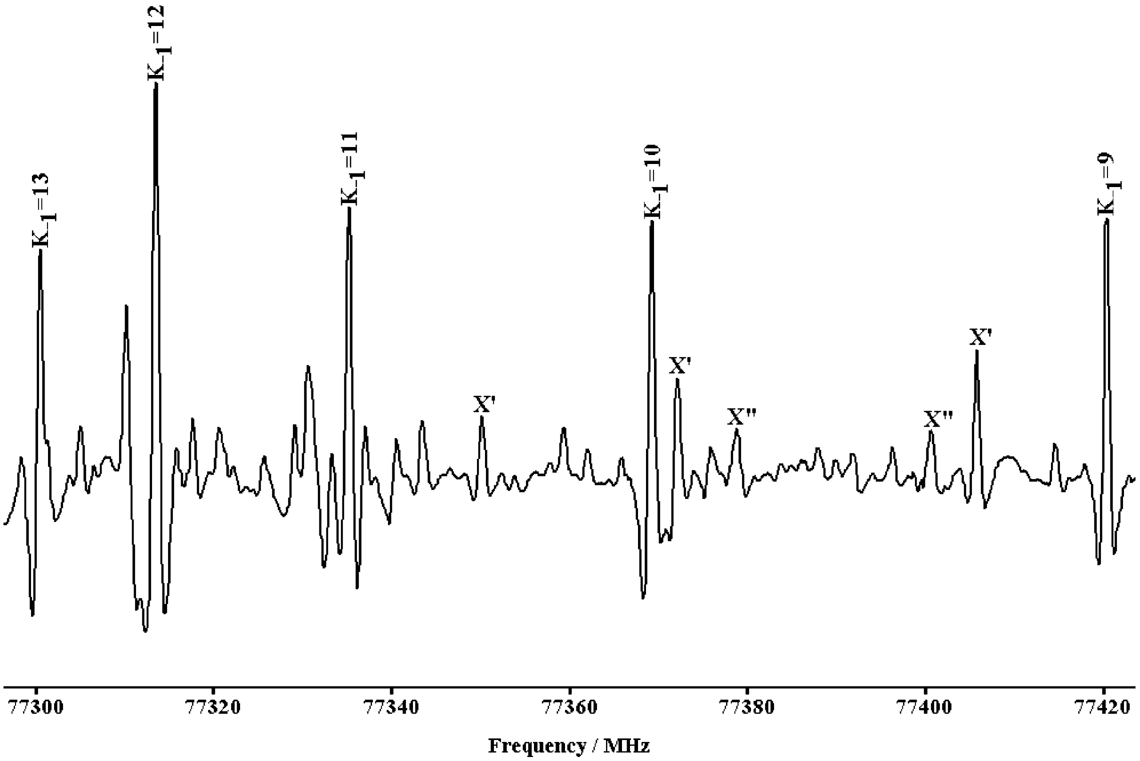


Figure 2. Section of spectrum showing transitions belonging to conformer V of 3-butyne-1-thiol. All transitions have $J = 17 \rightarrow 18$. Transitions marked X′ belong to the vibrationally excited-state V*a*1, while those marked X″ belong to V*a*2.

difficult to modulate, and they will, therefore, be significantly weaker than high- K_a lines for a given value of J. The failure to assign any c-type transitions is perhaps more surprising, as the values of μ_a and μ_c obtained from the B3LYP density functional theory calculation have similar magnitudes. These values are, however, estimates, and the value of μ_c prediction in this way could represent a significant overestimate. Additionally, the spectral complexity and lack of obvious "pile-ups" of transitions in the c-type spectrum, combined with the low population of conformer II, could explain the difficulty in identifying these transitions.

Since transitions in the ground-state spectrum of conformer II had been assigned, the RFWMDR experiment was once more employed in an attempt to detect transitions belonging to vibrationally excited states of this conformer. However, the excited-state spectra were too weak to be assigned, owing to a low population of conformer II.

Deuterated Isotopomers. The ground-state rotational spectrum of the isotopomer $HC{\equiv}CCH_2CH_2SD$ was measured using a deuterium enriched sample of 3-butyne-1-thiol prepared according to the procedure outlined above. Transitions corresponding to the deuterated forms of conformers II and V were observed. A total of 60 a-type, R-branch transitions were identified as belonging to the deuterated form of conformer II, while 101 a-type and b-type transitions were assigned to conformer V. The least-squares fits of these transitions gave the spectroscopic constants included in Table 3. The observed rotational transition frequencies for these spectra are presented in the Supporting Information in Tables 2S and 4S, together with the residual errors from the final cycle of the least-squares fits.

Failure to Detect Conformers I, III, and IV. Once the spectra attributable to conformers II and V were assigned, attempts were made to identify transitions in the spectra of the remaining three conformers of 3-butyne-1-thiol. No transitions were identified that could be assigned to any of these three conformers, despite the use of RFMWDR experiments to perform careful searches of the frequency ranges in which transitions were predicted by the rotational constants obtained from the quantum-chemical calculations for each conformer. A number of weaker transitions were observed that were not assigned to any species, as can be seen in Figure 2. It is believed that these transitions belong to further vibrationally excited states of conformers II and V or to impurities in the sample.

Energy Difference Between Conformers II and V. As mentioned above, the relative energy differences between the five conformers of 3-butyne-1-thiol were calculated by use of various quantum-chemical methods, giving the results listed in Table 2. An attempt was made to evaluate directly the energy difference between conformers II and V, which had been spectroscopically observed, by means of relative intensity measurements. A Boltzmann distribution of population among the two conformers and equal statistical weights for each of them was assumed. The values of the principal-axis components of the molecular electric dipole moment from calculations at the B3LYP/6-311++G(3df,2pd) level of theory were also employed. By use of this method, conformer II was found to be higher in energy than conformer V by 1.7 kJ mol^{-1}, and the estimated one standard deviation associated with this value is estimated to be of the order of ± 0.4 kJ mol^{-1}. This relatively large uncertainty arises owing to inaccuracies in measuring the height of transitions, because the spectral baseline is not clearly defined in all cases. Additionally, the congested nature of the spectrum of conformer II, where a-type, R-branch transitions occur in "pile ups", tends to increase the incidence of transitions overlapping. This in turn could lead to an apparent increase in the intensity of certain transitions in the spectrum of conformer II, thus lowering the energy difference derived from relative intensity measurements. It is therefore considered possible that the energy difference quoted above represents an underestimate.

Substitution Coordinates of Atoms in 3-Butyne-1-thiol. The position of an atom in a molecule may be determined by isotopic substitution of that atom. By solving Kraitchman's equations[34] with the equilibrium moments of inertia of the parent and substituted isotopomers, the coordinates of the substituted atom in the principal inertial axis system of the parent isotopomer can be calculated. For the case of a nonplanar asymmetric rotor, Kraitchman's equations take the form

$$|\alpha_s| = \left(\frac{\Delta P_\alpha}{\mu}\right)\left\{1 + \frac{\Delta P_\beta}{(I_\alpha - I_\beta)}\right\}\left\{1 + \frac{\Delta P_\gamma}{(I_\alpha - I_\gamma)}\right\}$$

where α_s is the principal axis coordinate of the substituted atom, $\Delta P_\alpha = (-\Delta I_\alpha + \Delta I_\beta + \Delta I_\gamma)$, and $\Delta I_\alpha = I'_\alpha - I_\alpha$. The position of a nucleus relative to the three principal inertial axes can be evaluated by cyclically permuting α, β, and γ over a, b, and c. It should be noted that this equation gives the modulus of the coordinates of an atom. While experimental values for the equilibrium moments of inertia were not determined during the course of the present investigation, solving Kraitchman's equations with ground-state moments of inertia will yield the substitution (r_s) coordinates of the substituted atom.

TABLE 5: Principal Axis Coordinates (pm) of the Thiol H Atom in 3-Butyne-1-thiol

experimental r_s coordinates[a]		ab initio r_e coordinates[b]	
$\|a_s\|$	48.0	a_e	58.5
$\|b_s\|$	144.4	b_e	−140.9
$\|c_s\|$	19.6	c_e	14.2

[a] See text for method used to determine r_s coordinates. [b] From an ab initio geometry optimization at the MP2/aug-cc-pVTZ level of theory.

This procedure was carried out using the ground-state moments of inertia obtained from the spectra of parent and deuterated isotopomers of conformer V, giving the magnitudes of the principal axis coordinates of the H atom belonging to the thiol group, which are reported in Table 5. Also reported in Table 5 are the principal axis coordinates of the thiol H atom, as predicted in the ab initio calculation at the MP2/aug-cc-pVTZ level of theory.

For the case of conformer II, in which only a-type transitions were detected, the error associated with the A_0 rotational constant, and, consequently, the principal moment of inertia I_a, is large. Therefore, the estimates of the substitution coordinates along the b and c principal inertial axes possess a large uncertainty, and only the a coordinate will be considered. The magnitude of the r_s a-coordinate obtained for the thiol H atom is 205.7 pm, while the corresponding r_e value, from an ab initio calculation at the MP2/aug-cc-pVTZ level of theory, is 210.8 pm.

While care should be taken when making comparisons between r_e and r_s structures, the differences between these sets of parameters are, in general, small, and in the present case, the agreement between experimentally determined r_s values and ab initio r_e values is close enough to confirm the assignment of observed microwave spectra to conformers II and V. It should be noted that discrepancies between r_e and r_s structures occur when the r_s coordinates are obtained by the substitution of the deuterium atom, as such a substitution will lead to changes in the zero-point motion of the molecule, and that Kraitchmann's method can produce anomalous results when the magnitude of a coordinate is small, that is, when an atom lies close to one of the principal inertial axes.[35,36]

Intramolecular Hydrogen Bonding. In recent investigations into intramolecular hydrogen bonding,[37,38] the close agreement (typically of the order of 2%) between experimental ground-state rotational constants and ab initio equilibrium values

TABLE 6: Geometry of Conformer V of 3-Butyne-1-thiol from an Ab Initio Optimization at the MP2/aug-cc-pVTZ Level of Theory

bond lengths (pm)		bond angles (deg)		dihedral angles (deg)	
$r(S-C_1)$	181.6	$\angle(H_1,S,C_1)$	95.3	$\angle(H_1,S,C_1,H_2)$	66.3
$r(C_1-C_2)$	152.9	$\angle(S,C_1,H_2)$	109.7	$\angle(H_1,S,C_1,H_3)$	−177.4
$r(C_2-C_3)$	145.9	$\angle(S,C_1,H_3)$	105.1	$\angle(H_1,S,C_1,C_2)$	−57.6
$r(C_3-C_4)$	121.6	$\angle(S,C_1,C_2)$	113.2	$\angle(S,C_1,C_2,H_4)$	−56.9
$r(S-H_1)$	133.9	$\angle(C_1,C_2,H_4)$	109.4	$\angle(S,C_1,C_2,H_5)$	−174.5
$r(C_1-H_2)$	108.9	$\angle(C_1,C_2,H_5)$	109.1	$\angle(S,C_1,C_2,C_3)$	64.6
$r(C_1-H_3)$	109.0	$\angle(C_1,C_2,C_3)$	111.6	$\angle(C_1,C_2,C_3,C_4)$	2.2
$r(C_2-H_4)$	109.1	$\angle(C_2,C_3,C_4)$	177.6	$\angle(C_2,C_3,C_4,H_6)$	177.2
$r(C_2-H_5)$	109.3	$\angle(C_3,C_4,H_6)$	178.8		
$r(C_4-H_6)$	106.2				

calculated by geometry optimizations at the MP2/aug-cc-pVTZ level of theory was interpreted as an indication that the ab initio structures represented a good approximation of the molecular geometries. Of the two conformers of 3-butyne-1-thiol detected by spectroscopic means, the potential for intramolecular hydrogen bonding exists in conformer V only. While the agreement between the experimental rotational constants and those obtained for this conformer from an MP2/aug-cc-pVTZ geometry optimization was not as close as it had been for the cases mentioned above, the differences were still less than 3% for each of the rotational constants. The structure from the MP2/aug-cc-pVTZ geometry optimization (Table 6 and Figure 1) is therefore still likely to be a useful approximation to the structure of conformer V. When considering the possibility of intermolecular hydrogen bonding in 3-butyne-1-thiol, a parameter of particular interest is the distance between the H atom of the thiol group and the center of the $C3\equiv C4$ triple bond. The distance obtained for this parameter from the MP2/aug-cc-pVTZ geometry is 275 pm, while the sum of the van der Waals radii of the groups involved is 290 pm.[1] This apparent reduction in the distance between these two groups, relative to the sum of their van der Waals radii, suggests that conformer V is, indeed, stabilized by an intramolecular hydrogen bond between the thiol group and the π-electrons of the $C3\equiv C4$ triple bond. In addition, the fact that the lowest-energy conformer is one in which the formation of an intramolecular hydrogen bond is possible suggests that a stabilizing hydrogen bond is formed in this conformer.

It was noted above that the closely related molecules 3-butyne-1-ol ($HC\equiv CCH_2CH_2OH$)[12] and 3-butyne-1-amine ($HC\equiv CCH_2CH_2NH_2$)[13] have been found to be stabilized by intramolecular hydrogen bonding in their lowest-energy conformers. These conformers possess analogous structures to conformer V of 3-butyne-1-thiol, indicating a general propensity for the formation of hydrogen bonds to the π-electron density associated with the $C\equiv C$ triple bond in these molecules.

The conformational properties of $HC\equiv CCH_2CH_2SH$ and internal hydrogen bonding are also very similar to those found in 3-mercaptopropionitrile ($N\equiv CCH_2CH_2SH$).[7] The energy difference between the heavy-atom synclinal and antiperiplanar forms of 3-mercaptopropionitrile is 1.3(2) kJ/mol[7] favoring the hydrogen-bonded conformer, compared with 1.7(4) kJ/mol for the title compound.

Conclusions

The microwave spectrum of 3-butyne-1-thiol was recorded in the 12−80 GHz frequency range, by means of Stark-modulation microwave spectroscopy. Rotational transitions observed in this frequency range were assigned to two conformers of the molecule. No spectra attributable to the remaining three conformers were detected. The rotational spectra of five vibrationally excited states of the lowest-energy conformer were assigned, and a tentative assignment of the individual vibrational states was made with the assistance of a DFT calculation.

A comparison was made between ground-state rotational constants derived from the experimental spectra and the corresponding equilibrium values obtained from an ab initio geometry optimization at the MP2/aug-cc-pVTZ level of theory. These constants were found to agree to within 3% in all cases, which represents a reasonable agreement between experiment and theory.

The relative energies of the five possible conformers of 3-butyne-1-thiol were calculated in a series of quantum-chemical calculations, and the energy difference between the two observed conformers was estimated by comparing the intensities of rotational transitions. The conformer consistently identified as being lowest in energy possessed a synclinal (formerly gauche) arrangement of the atoms $S-C1-C2-C3$. An analysis of the structure obtained for this conformer from the MP2/aug-cc-pVTZ geometry optimization suggests that this lowest-energy conformer is stabilized by an intramolecular hydrogen bond formed between the H atom of the thiol group and π-electron density associated with the $C3\equiv C4$ triple bond.

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Supporting Information Available: Assigned microwave spectra and additional results from quantum-chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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