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A Microwave Spectroscopic and Quantum Chemical Study of 3-Butyne-1-selenol ($HSeCH_2CH_2C{\equiv}CH$)

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The microwave spectrum of 3-butyne-1-selenol has been studied by means of Stark-modulation microwave spectroscopy and quantum chemical calculations employing the B3LYP/aug-cc-pVTZ and MP2/6-311++G-(3df,3pd) methods. Rotational transitions attributable to the $H^{80}SeCH_2CH_2C{\equiv}CH$ and $H^{78}SeCH_2CH_2C{\equiv}CH$ isotopologues of two conformers of this molecule were assigned. One of these conformers possesses an *antiperiplanar* arrangement for the atoms Se−C−C−C, while the other is *synclinal* and seems to be stabilized by the formation of a weak intramolecular hydrogen bond between the hydrogen atom of the selenol group and the π electrons of the C≡C triple bond. The energy difference between these conformers was determined to be 0.2(5) kJ/mol by relative intensity measurements, and the hydrogen-bonded form was slightly lower in energy.

Introduction

The ability of selenols to form intramolecular hydrogen bonds in the gas phase was first demonstrated in the case of 3-buteneselenol ($HSeCH_2CH_2C{=}CH_2$),[1] where the H atom of the selenol group forms an internal H bond with the π electrons of the double bond. It was recently found that the preferred conformer of cyclopropylmethaneselenol ($C_3H_5CH_2SeH$)[2] is stabilized by a very weak H bond between the selenol group and the pseudo-π electrons[3] along the edge of the cyclopropyl ring.

The subject of the current study, namely, 3-butyne-1-selenol ($HSeCH_2CH_2C{\equiv}CH$), has been chosen to allow a direct comparison of the hydrogen-bonding abilities in the analogous alcohol ($HOCH_2CH_2C{\equiv}CH$),[4,5] thiol ($HSCH_2CH_2C{\equiv}CH$),[6] and amine ($H_2NCH_2CH_2C{\equiv}CH$),[7] all of which are stabilized by intramolecular hydrogen bonding involving the π electrons of the triple bond in their lowest-energy conformers. A model of 3-butyne-1-selenol with atom numbering is shown in Figure 1. Rotation about the C3−C4 and C4−Se5 bonds may produce rotational isomerism. A total of five conformers that can in principle be identified by MW spectroscopy are depicted in the same figure and are given Roman numerals for reference. The C2−C3−C4−Se5 chain of atoms is *antiperiplanar* (obsolete "*trans*") in conformers **I** and **II**, and −*synclinal* (obsolete "−*gauche*") in the remaining three forms. The C3−C4−Se5−H11 link of atoms is *antiperiplanar* in **I** and **III**, −synclinal in **II** and **V**, and +*synclinal* in **IV**. Mirror-image forms, which would have identical MW spectra, exist for all rotamers but **I**, which has a symmetry plane. The H atom of the selenol group is brought into relatively close proximity with the π electrons of the triple bond in only one conformer, namely **IV**.

The title compound has very recently been investigated by photoelectron spectroscopy and quantum chemical calculations, but no definite information about the conformational properties was obtained in this study.[8]

A successful investigation of a delicate conformational equilibrium such as the one presented by gaseous 3-butyne-1-selenol requires experimental methods possessing high resolution. MW spectroscopy meets this requirement because of its superior accuracy and resolution, making this method especially well suited for conformational studies of gaseous species. The spectroscopic work has been augmented by high-level quantum chemical calculations, which were conducted with the purpose of obtaining information for use in assigning the MW spectrum and investigating properties of the potential-energy hypersurface.

This work represents a continuation of our studies of intramolecular hydrogen bonding, of which 4-pentyn-1-ol ($HO(CH_2)_3C{\equiv}CH$),[9] trifluorothioacetic acid (CF_3COSH),[10] (*Z*)-3-mercapto-2-propenenitrile ($HSCH{=}CHC{\equiv}N$),[11] (*Z*)-3-amino-2-propenenitrile ($H_2NCH{=}CHC{\equiv}N$),[12] 3-butynethiol ($HSCH_2CH_2C{\equiv}CH$),[6] (methylenecyclopropyl)methanol ($H_2C{=}C_3H_3CH_2OH$),[13] cyclopropylmethaneselenol ($C_3H_5CH_2SeH$),[2] 2-chloroacetamide ($CH_2ClCONH_2$),[14] 1,1,1-trifluoro-2-propanol ($CF_3CH(OH)CH_3$),[15] cyclopropylmethylphosphine ($C_3H_5CH_2PH_2$),[16] and 1-fluorocyclopropanecarboxylic acid (C_3H_4FCOOH)[17] are recent examples. Less recent work on gas-phase studies of intramolecular hydrogen bonding is reviewed elsewhere.[18,19]

Experimental Section

Caution: 3-Butynylselenocyanate and 3-butyne-1-selenol are malodorous and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.

Synthesis of 3-Butyne-1-selenol. The already reported synthesis of 3-butyne-1-selenol[20] has been slightly modified. The compound has been prepared by a chemoselective reduction of 3-butynylselenocyanate (selenocyanic acid, 3-butyn-1-yl ester).

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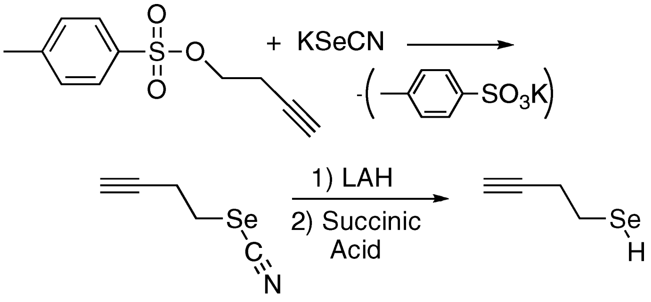
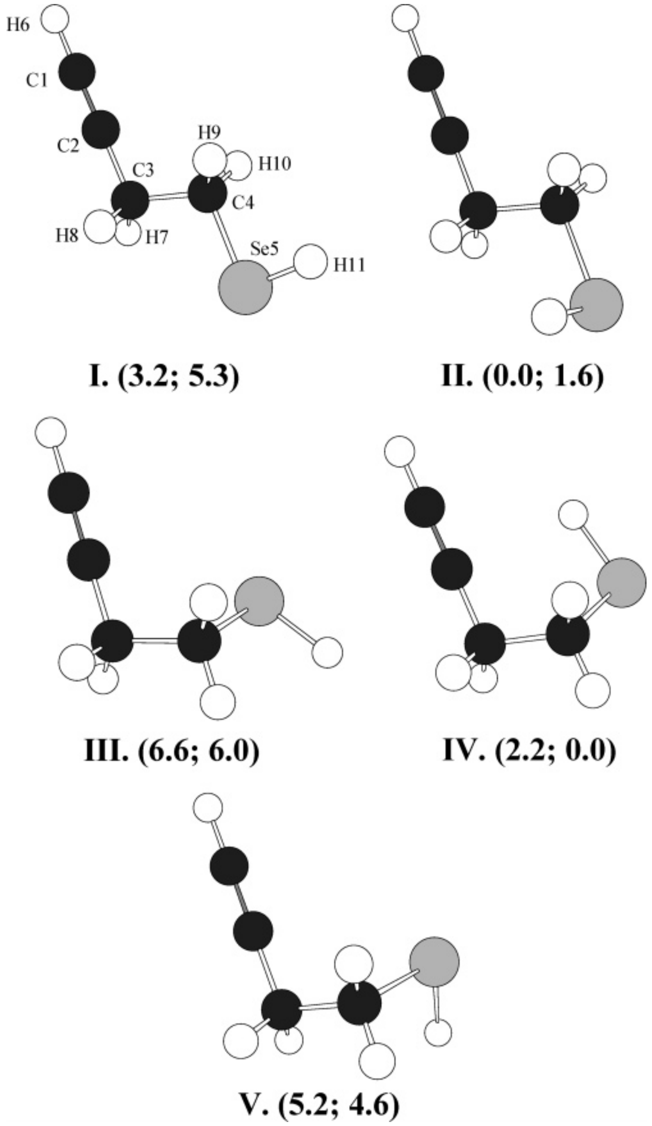


Selenocyanic Acid, 3-Butyn-1-yl Ester. In a 100-mL two-necked flask equipped with a stirring bar and a nitrogen inlet were introduced 3-butyn-1-yl *p*-toluenesulfonate[21] (4.48 g, 20 mmol), acetonitrile (40 mL), and potassium selenocyanate (2.88 g, 20 mmol). After the mixture was stirred for 3 h at 60 °C, the precipitated potassium *p*-toluenesulfonate was filtered and the solvent was removed in vacuum. Selenocyanic acid, 3-butyn-1-yl ester, was purified by distillation in vacuum. Yield: 2.62 g (83%). Bp: 51 °C (0.1 mmHg).

3-Butyne-1-selenol. The apparatus previously described for the preparation of propargylphosphine was used.[22] A 100-mL two-necked flask containing a suspension of succinic acid (4.72 g, 40 mmol) in tetraglyme (30 mL) was immersed in a 0 °C cold bath, attached to a vacuum line, and degassed. In a 50-mL two-necked flask equipped with a stirring bar and a nitrogen inlet were introduced LAH (200 mg, 5.3 mmol) and tetraglyme (10 mL). The flask was immersed in a bath cooled at 0 °C, and the 3-butyneselenocyanate (0.79 g, 5 mmol) diluted in tetraglyme (5 mL) was slowly added. After being stirred for 10 min, 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, the selenol was distilled off in vacuum (10^{-1} mbar) from the reaction mixture. The first cold trap (-30 °C) removed selectively the less volatile products, and the selenol was condensed in a second trap cooled at -70 °C. At the end of the reaction, the second trap was disconnected from the vacuum line and attached to the microwave spectrometer. Yield: 0.605 g, (91%). Bp ≈ -40 °C (0.1 mmHg). This compound was stable for days in pure form in a cold room (-30 °C) or diluted in a solvent ($CDCl_3$) at room temperature. ^{1}H NMR ($CDCl_3$): δ -0.24 (t, 1H, $^3J_{HH} = 7.1$ Hz, SeH, $^1J_{SeH} = 46.3$ Hz (d)); 2.10 (t, 1H, $^4J_{HH} = 2.5$ Hz, C≡CH); 2.67 (td, 2H, $^3J_{HH} = 5.9$ Hz, $^4J_{HH} = 2.5$ Hz, $C{\equiv}CCH_2$); 2.73 (dt, 1H, $^3J_{HH} = 7.1$ Hz, $^3J_{HH} = 5.9$ Hz, CH_2Se). ^{13}C NMR ($CDCl_3$): δ 15.7 ($^1J_{CH} = 128.5$ Hz (t), $SeCH_2$); 23.7 ($^1J_{CH} = 130.9$ Hz (t), $C{\equiv}C\mathit{C}H_2$); 69.8 ($^1J_{CH} = 249.0$ Hz (d), $C{\equiv}\mathit{C}H$); 82.7 ($^2J_{CH} = 45.0$ Hz (d), $HC{\equiv}\mathit{C}$). ^{77}Se NMR ($CDCl_3$): δ -0.17.

Microwave Experiment. The spectrum of 3-butyne-1-selenol was recorded in the 40−80 GHz frequency interval by Stark-modulation spectroscopy, using the microwave spectrometer of the University of Oslo, which measures the frequency of individual transitions with an estimated accuracy of ~0.10 MHz. Details of the construction and operation of this spectrometer have been given elsewhere.[17,23] While recording the spectrum, the Stark cell was cooled to approximately -15 °C with solid CO_2, in an attempt to increase the intensity of the spectrum. Further cooling of the Stark cell was not possible in this case because of the low vapor pressure of 3-butyne-1-selenol. Radio frequency microwave double-resonance experiments, similar to those performed by Wodarczyk and Wilson,[24] were also conducted to assign unambiguously particular transitions. Attempts were made to produce the deuterated species $DSeCH_2CH_2C{\equiv}CH$ by mixing fumes of $HSeCH_2CH_2C{\equiv}CH$ with fumes of D_2O in the microwave cell. Surprisingly, no exchange of the H atom of the selenol group with D was registered.



I. (3.2; 5.3)

II. (0.0; 1.6)

III. (6.6; 6.0)

IV. (2.2; 0.0)

V. (5.2; 4.6)

Figure 1. Five stable rotameric forms of 3-butyne-1-selenol according to the quantum chemical calculations. Atom numbering is given on conformer **I**. Calculated relative energies (B3LYP left; MP2 right) are indicated underneath each conformer. Microwave spectra of **II** and **IV** were assigned. Conformer **IV** was found to be slightly more stable than **II** by 0.2(5) kJ/mol by relative intensity measurements.

Results

Quantum Chemical Calculations. A series of quantum chemical calculations were conducted on 3-butyne-1-selenol, with the purpose of obtaining information for use in assigning the spectrum and investigating structures of the five “stable” conformers, associated with minima on the potential-energy hypersurface of this molecule. All calculations were performed using the Gaussian 03 suite of programs,[25] running on the 64 processor “superdome” computer of the University of Oslo.

Geometry optimizations were carried out on the five possible rotameric forms of 3-butyne-1-selenol, 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 density functional theory (DFT), as well as second-order Møller-Plesset perturbation theory (MP2).[26] The DFT calculations were performed using

TABLE 1: B3LYP[a] and MP2[b] Structures of the Five Stable Conformers[c] of $HSeCH_2CH_2C{\equiv}CH$

	I		II		III		IV		V	
conformer	B3LYP	MP2	**B3LYP**	**MP2**	B3LYP	MP2	**B3LYP**	**MP2**	B3LYP	MP2
bond length (pm)										
C1−C2	119.9	121.5	**120.0**	**121.5**	119.9	121.5	**119.9**	**121.5**	119.9	121.4
C1−H6	106.1	106.2	**106.1**	**106.2**	106.1	106.2	**106.1**	**106.2**	106.1	106.2
C2−C3	145.8	145.9	**145.9**	**146.0**	145.9	145.9	**145.8**	**145.8**	145.7	145.8
C3−C4	153.2	152.8	**153.3**	**152.8**	153.1	152.7	**153.3**	**152.9**	153.3	152.9
C3−H7	109.3	109.2	**109.2**	**109.0**	109.2	109.1	**109.2**	**109.1**	109.2	109.1
C3−H8	109.3	109.2	**109.2**	**109.1**	109.5	109.2	**109.5**	**109.3**	109.6	109.3
C4−Se5	198.7	195.7	**197.8**	**195.1**	199.1	196.2	**197.8**	**195.1**	198.0	195.2
C4−H9	108.6	108.7	**108.6**	**108.7**	108.6	108.7	**108.8**	**108.9**	108.7	108.7
C4−H10	108.6	108.7	**108.8**	**108.9**	108.6	108.7	**108.6**	**108.7**	108.8	108.9
Se5−H11	147.1	146.0	**147.3**	**146.2**	147.2	146.1	**147.1**	**146.2**	147.3	146.2
H11···C1[d]	606.9	602.5	**562.2**	**554.8**	540.5	523.1	**330.8**	**304.4**	499.8	481.7
H11···C2[d]	504.4	499.8	**448.9**	**440.3**	458.2	446.3	**294.6**	**273.2**	409.8	393.4
angles (deg)										
C2−C3−C4	111.7	110.7	**111.8**	**110.8**	113.8	111.9	**113.7**	**112.0**	114.1	112.3
C2−C3−H7	109.3	109.7	**109.8**	**110.2**	109.3	109.4	**109.4**	**109.6**	109.5	109.7
C2−C3−H8	109.4	109.6	**109.4**	**109.7**	108.9	109.4	**108.6**	**109.1**	108.7	109.2
C4−C3−H7	109.8	109.8	**109.6**	**109.5**	109.6	109.5	**109.7**	**109.6**	109.8	109.7
C4−C3−H8	109.8	109.8	**109.7**	**109.6**	108.2	109.0	**108.2**	**108.9**	108.0	108.7
H7−C3−H8	106.6	107.2	**106.4**	**106.9**	106.8	107.6	**106.7**	**107.7**	106.3	107.1
C3−C4−Se5	109.0	108.1	**113.7**	**112.8**	111.5	109.7	**115.0**	**113.5**	115.3	113.9
C3−C4−H9	110.7	110.3	**111.4**	**111.0**	109.9	110.0	**109.8**	**110.0**	110.4	110.7
C3−C4−H10	110.7	110.3	**110.8**	**110.4**	110.9	110.5	**111.2**	**110.8**	110.7	110.3
Se5−C4−H9	108.4	109.3	**108.4**	**109.2**	107.0	108.0	**103.8**	**104.8**	107.4	108.3
Se5−C4−H10	108.5	109.3	**104.3**	**105.1**	108.1	109.0	**108.2**	**109.0**	104.4	105.0
H9−C4−H10	109.5	109.6	**108.0**	**108.1**	109.3	109.6	**108.4**	**108.6**	108.2	108.3
C4−Se5−H11	94.9	95.0	**95.3**	**94.5**	94.4	94.3	**95.0**	**93.8**	94.9	94.2
C2−C1−H6	179.6	179.5	**179.5**	**179.4**	180.2	180.0	**179.7**	**179.3**	180.0	180.1
C1−C2−C3	178.8	178.1	**178.5**	**177.6**	179.3	178.1	**179.4**	**178.3**	179.4	178.7
dihedral angle (deg)										
C1−C2−C3−C4	−0.4	−0.1	**1.3**	**0.5**	−10.9	2.7	**−37.7**	**−10.6**	−55.2	−39.4
C3−C2−C1−H6	−179.9	−178.0	**176.4**	**176.8**	90.1	97.5	**−162.2**	**−172.8**	162.0	147.2
C2−C3−C4−Se5	−179.9	179.9	**−178.0**	**−178.3**	−62.2	−59.0	**−68.8**	**−65.8**	−67.0	−64.6
C2−C3−C4−H9	61.0	60.5	**59.3**	**58.7**	179.3	−177.7	**174.5**	**177.2**	171.1	173.1
C2−C3−C4−H10	−60.2	−60.7	**−60.9**	**−61.1**	58.3	61.2	**54.6**	**57.2**	51.3	53.2
H7−C3−C4−Se5	−58.3	−58.9	**−56.0**	**−56.6**	60.6	62.5	**54.2**	**56.0**	56.5	57.7
H7−C3−C4−H9	−177.5	−178.3	**−178.8**	**−179.6**	−57.9	−56.2	**−62.5**	**−61.0**	−65.5	−64.7
H7−C3−C4−H10	60.9	60.5	**61.1**	**60.6**	−178.9	−177.4	**177.6**	**179.0**	174.7	175.5
H8−C3−C4−Se5	58.6	58.7	**60.5**	**60.5**	176.6	179.9	**170.3**	**173.5**	172.0	174.5
H8−C3−C4−H9	−60.6	−60.7	**−62.3**	**−62.5**	58.1	61.2	**53.6**	**56.5**	50.0	52.1
H8−C3−C4−H10	177.8	178.1	**177.6**	**177.7**	−62.8	−59.9	**−66.3**	**−63.5**	−69.7	−67.7
C3−C4−Se5−H11	−179.0	179.7	**−67.9**	**−65.7**	−146.8	−151.5	**62.3**	**58.6**	−76.8	−73.7
H9−C4−Se5−H11	−58.4	−60.2	**56.5**	**58.3**	−26.6	−31.6	**−177.7**	**178.5**	46.7	50.0
H10−C4−Se5−H11	60.4	59.7	**171.4**	**174.0**	91.1	87.5	**−62.7**	**−65.4**	161.5	165.5

[a] Basis set: aug-cc-pVTZ. [b] Basis set: 6-311++G(3df,3pd). [c] The microwave spectra of the conformers marked in bold face have been assigned. [d] Nonbonded distance.

Dunning's extensive aug-cc-pVTZ basis set,[27,28] which is optimized for selenium.[28] This basis set is of triple-ζ quality and includes polarized functions for valence electrons and is augmented by diffuse functions. DFT optimizations were undertaken employing the B3LYP hybrid functional[29,30] in conjunction with the aug-cc-pVTZ basis set using the default convergence criteria of Gaussian 03. The approximate equilibrium structures of conformers **I**−**V** obtained in these calculations are shown in Table 1. The nonbonded distances between H11 and C1 and between H11 and C2 are also listed for each rotamer.

None of the vibrational frequencies, which were calculated for each rotamer, were imaginary, implying that these five forms are minima on the potential-energy hypersurface. The rotational constants calculated from these structures are shown in Table 2, together with Watson's A-reduction quartic centrifugal distortion constants,[31] the components of the dipole moment along the principal inertial axes, the total dipole moment, and the energy differences relative to the energy of the global minimum conformer, which turned out to be **II** in these B3LYP/aug-cc-pVTZ calculations. The B3LYP energy differences have been corrected for zero-point vibrational energies and are also shown on Figure 1 (first number in the parentheses).

Analogous MP2 calculations were also carried out. These calculations are considerably more expensive than B3LYP calculations with the same basis set, and a smaller basis set than aug-cc-pVTZ had to be used owing to the available computational resources. The 6-311++G(3df,3pd) basis set,[32] which is also of triple-ζ quality, includes polarized functions for the valence electrons and is augmented with diffuse functions was therefore selected. The results of these calculations, together with the B3LYP results, are included in Tables 1 and 2. Conformer **IV** was found to be the global minimum in the MP2 calculations, which contrasts the B3LYP result above, where **II** was found to be the global minimum. The MP2 energies relative to **IV** are shown in Table 2 and in Figure 1 (second number in the parentheses).

Some of the results listed in Tables 1 and 2 warrant further comments. Interestingly, the B3LYP and MP2 bond lengths (Table 1) are similar within a few tenths of a picometer with some exceptions, namely the C1≡C2 triple bond, which is about

TABLE 2: B3LYP[a] and MP2[b] Parameters of the Five Stable Conformers[c] of $H^{80}SeCH_2CH_2C{\equiv}CH$

	I		II		III		IV		V	
conformer:	B3LYP	MP2	**B3LYP**	**MP2**	B3LYP	MP2	**B3LYP**	**MP2**	B3LYP	MP2
rotational constants (MHz)										
A	24422.6	24151.8	**24181.5**	**23828.1**	6541.6	6251.3	**6949.9**	**6644.8**	6900.9	6639.8
B	1002.9	1023.0	**985.2**	**1004.8**	1633.4	1780.3	**1520.8**	**1637.5**	1511.1	1612.9
C	975.0	993.5	**964.2**	**982.1**	1368.8	1456.0	**1306.8**	**1379.6**	1306.6	1372.5
quartic centrifugal distortion constants (kHz)										
Δ_J	0.0739	0.0751	**0.0672**	**0.0697**	1.65	1.78	**0.980**	**0.956**	1.05	1.15
Δ_{JK}	−3.03	−3.56	**−3.48**	**−4.19**	−14.1	−12.1	**−10.3**	**−7.81**	−11.2	−10.1
Δ_K	194	219	**254**	**283**	43.9	30.8	**41.9**	**27.5**	45.6	34.9
δ_J	0.00339	0.003 80	**0.00315**	**0.00367**	0.447	0.510	**0.244**	**0.247**	0.257	0.293
δ_K	0.219	0.338	**0.205**	**0.309**	3.53	3.35	**2.43**	**2.14**	2.53	2.46
dipole moment[d] (10^{-30} C m)										
μ_a	1.8	2.0	**2.3**	**2.8**	0.8	0.6	**3.0**	**3.5**	1.4	1.6
μ_b	2.4	3.0	**0.1**	**0.1**	5.6	6.0	**3.4**	**3.6**	5.1	5.5
μ_c	0.0[e]	0.0[e]	**1.4**	**1.7**	0.9	1.3	**1.1**	**1.3**	0.5	0.6
μ_{tot}	3.0	3.6	**2.7**	**3.2**	5.7	6.2	**4.6**	**5.2**	5.3	5.8
energy difference[f] (kJ/mol)										
ΔE	3.2	5.3	**0.0**[g]	**1.6**	6.6	6.0	**2.2**	**0.0**[h]	5.2	4.6

[a] Basis set: aug-cc-pVTZ. [b] Basis set: 6-311++G(3df,3pd). [c] The microwave spectra of the conformers, whose parameters are marked in bold face, have been assigned. [d] 1 D = 3.33564×10^{-30} C m. [e] For symmetry reasons. [f] Corrected for harmonic zero-point energies. [g] Minimum in the B3LYP calculations. The B3LYP energy of this rotamer corrected for harmonic zero-point energy is −6 714 915.32 kJ/mol. [h] Minimum in the MP2 calculations. The MP2 energy of this rotamer corrected for harmonic zero-point energy is −6 709 423.48 kJ/mol.

2 pm longer in the MP2 calculations, the C4−Se5 bond, which is approximately 3 pm shorter in the MP2 procedure, and Se5−H11 bond, which is shorter by about 1 pm in the MP2 calculations.

Experimental C−Se and Se−H bond lengths of related compounds have been reported. The r_0 C−Se bond length in CH_3SeH is 195.9 pm.[33] The r_s bond length in the C−C−Se−H *synclinal* conformer of CH_3CH_2SeH is 195.7(4) pm, and 196.2(2) pm in the *antiperiplanar* form.[34] Table 1 shows that the experimental distances are much closer to the MP2 predictions than to the B3LYP results. The Se−H bond length is 147.3 pm in CH_3SeH,[33] 146.7(4) pm in the C−C−Se−H *synclinal* form, and 144.0(10) pm in the *antiperiplanar* conformation of CH_3CH_2SeH.[34] These experimental results are not far from the theoretical predictions in Table 1.

The two methods predict bond angles to be rather similar. The largest discrepancies are found for the bond angles associated with the selenol group, where deviations ∼1.5° are seen (Table 1). Even larger differences are calculated for the dihedral angles in some cases. It is especially noted that the important C2−C3−C4−Se5 and C3−C4−Se5−H11 dihedral angles are 3.0 and 3.7°, respectively, smaller in conformer **IV** in the MP2 than in the B3LYP calculations. This brings the H atom of the selenol group into closer proximity with the π electrons of the triple bond in the MP2 than in the B3LYP structure, as can be seen in the nonbonded H11···C1 and H11···C2 distances (Table 1). Interestingly, conformer **IV**, which has the smallest distance between the H atom of the selenol group and the triple bond, is found to be the favored form by the MP2 method.

Some of the quartic centrifugal distortion constants predicted by the two methods vary quite considerably (Table 2). This is not surprising since they depend on the second derivative at the minima of the potential-energy hypersurface. The B3LYP dipole moments (same table) are generally somewhat smaller than their MP2 counterparts, which is typical.

The calculated energy differences are presumably uncertain by several kilojoules per mole. The fact that both methods find that all five rotameric forms fall within a rather narrow range of <7 kJ/mol (Table 2) makes it likely that more than one form might be present in the gas at −15 °C in such high concentrations that it might be possible to assign their MW spectra and experimentally determine the energy difference(s).

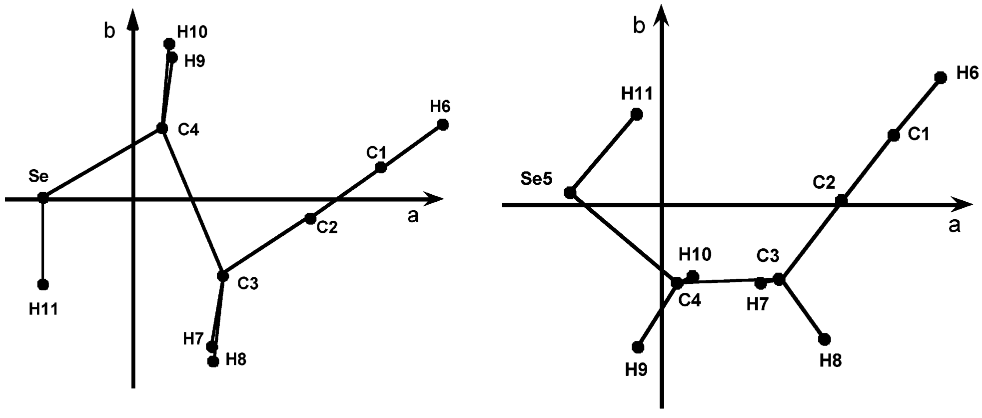
Finally, it should be mentioned that the energy differences previously[8] obtained in MP2 as well as in B3LYP calculations using the cc-pVTZ basis set are very similar to their counterparts reported in Table 2.

Microwave Spectrum and Assignment of the $H^{80}SeCH_2CH_2C{\equiv}CH$ Isotopologue of Conformer II. A projection of this rotamer in the $a-b$ principal axis plane is shown in Figure 2. This rotamer is predicted to have a relatively small dipole moment with its major component along the *a*- and *c*-inertial axes (Table 2). The small dipole moment is unfortunate, since the intensity of the MW spectrum depends on the square of the dipole moment components.

The intensity of the spectrum also depends on the partition function, which governs the population of each quantum state. Two of the rotational constants (B and C) are predicted to be relatively small for this rotamer (Table 2). Moreover, the quantum chemical calculations above indicate that there are three vibrational fundamentals with frequencies below 200 cm^{-1}, and three more with frequencies between 200 and 500 cm^{-1} (not given in Table 1 or 2) for each rotamer. A comparatively large partition function and a low population of each quantum state are therefore expected at ∼−15 °C.

Another factor that contributes negatively to the intensity is the fact that selenium has six naturally occurring isotopes, of which five are relatively abundant (^{76}Se (9.0%), ^{77}Se (7.6%), ^{78}Se (23.5%), ^{80}Se (49.8%), and ^{82}Se (9.2%)), which means that the intensity is reduced accordingly. The presence of relatively large concentrations of rotameric forms other than **II** would have a similar effect on the intensity.

Survey spectra of 3-butyne-1-selenol revealed a comparatively weak and very crowded spectrum with absorption lines occurring every few megahertz throughout the 40−80 GHz spectral interval. The ^{80}Se isotopologue of conformer **II** is nearly a prolate rotor (Ray's asymmetry parameter[35] $\kappa = -0.996$), with μ_a as its major dipole moment component (Table 2). Pileups of ^{a}R-branch transitions separated by approximately $B + C \approx 1.9$ GHz were therefore expected in this spectral region. The high



II IV

Figure 2. Projection of conformers **II** and **IV** in their *a*−*b* principal inertial axes planes.

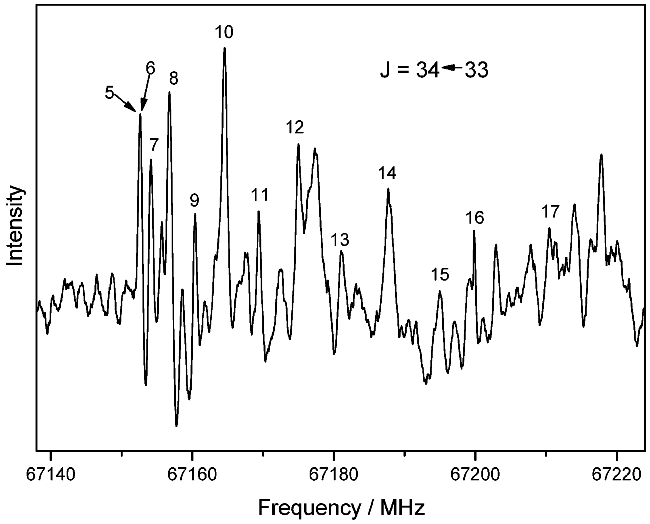


Figure 3. This portion of the MW spectrum of 3-butyne-1-selenol shows the *a*-type $J = 34 \leftarrow 33$ transition of the ground vibrational state of the $H^{80}SeCH_2CH_2C{\equiv}CH$ isotopologue of conformer **II**. The values of the coalescing K_{-1} lines are shown above each assigned lines. The $K_{-1} = 5$ and 6 lines overlap. The spectrum was recorded applying a Stark-modulation field strength of approximately 320 V/cm.

TABLE 3: Experimental Spectroscopic Constants[a] of the Ground Vibrational State of the $H^{80}SeCH_2CH_2C{\equiv}CH$[b] and $H^{78}SeCH_2CH_2C{\equiv}CH$[c] Isotopologues of Conformer II of 3-Butyne-1-selenol

species:	$H^{80}SeCH_2CH_2C{\equiv}CH$	$H^{78}SeCH_2CH_2C{\equiv}CH$
A (MHz)	19820[d]	20200[d]
B (MHz)	1002.840(45)	1010.37(11)
C (MHz)	972.139(45)	980.11(11)
Δ_J (kHz)	0.08242(51)	0.007769(37)
Δ_{JK} (kHz)	−3.6719(78)	−3.7569(61)
Δ_K (kHz)	254d	254[d]
δ_J (kHz)	0.00315[d]	0.00315[d]
δ_K (kHz)	0.205d	0.205[d]
Φ_{JK}[e] (Hz)	0.0358(32)	0.0[f]
rms[g]	1.3476	1.0474
no. of transitions	287	118

[a] A-reduction I^r representation.[31] Uncertainties represent one standard deviation. [b] Full spectrum in Table 1S in the Supporting Information. [c] Full spectrum in Table 2S in the Supporting Information. [d] Fixed; see text. [e] Further sextic distortion constants preset at zero. [f] Preset at zero. [g] Root-mean-square deviation.

K_{-1} members of these series are modulated at comparatively low Stark fields, which facilitate their assignments. Series of pileups were readily seen to protrude from the background of weaker transitions, when a relatively low Stark field was applied. A typical example is the pileup associated with the $J = 34 \leftarrow 33$ *a*-type transitions of the $H^{80}SeCH_2CH_2C{\equiv}CH$ species, which is shown in Figure 3.

These pileups were the key to the assignment of the MW spectrum of conformer **II**. It was found that pairs of ^aR-lines with identical $K_{-1} \geq 4$ coalesce, because $\kappa \approx -1$, and that transitions with different values of K_{-1} frequently overlap. A total of 287 ^aR-lines with $K_{-1} \geq 3$ were ultimately assigned. Definite assignments of transitions with $K_{-1} < 3$ could not be made primarily because these transitions are difficult to modulate and are often overlapped. Extensive searches for *c*-type lines were also made because a small μ_c component is predicted for conformer **II** (Table 2), but no such transitions were found. This is not surprising because the *c*-type lines should be rather weak according to the quantum chemical calculations, which would make it very difficult to assign them in the crowded spectrum observed for this compound.

The ^aR-spectrum of **II** was fitted to Watson's A-reduction Hamiltonian using the I^r-representation[31] employing Sørensen's program ROTFIT.[36] The spectrum is shown in Table 1S in the Supporting Information, and the spectroscopic constants of the ^{80}Se isotopologue are listed in Table 3.

The assigned ^aR-lines furnish insufficient information for an accurate determination of the *A* rotational constant and the Δ_K, δ_J, and δ_K centrifugal distortion constants for this near-prolate rotor. The three quartic centrifugal distortion constants were held fixed at the B3LYP values (Table 2) in the weighted least-squares fit. Only one of the sextic constants, namely Φ_{JK}, was fitted, while the others were fixed at zero. The *A* rotational constant, which was fixed at the value shown in Table 3, was estimated assuming that $I_c - I_a - I_b = -9.6 \times 10^{-20}$ u m^2, where I_a, I_b, and I_c are the principal moments of inertia. The value -9.6×10^{-20} u m^2 was obtained in both the MP2 and B3LYP calculations and should be fairly independent of the values of I_b and I_c.

The rotational constants of conformers **I** and **II** are so similar that a definite conformer assignment cannot be made on the basis of the rotational constants alone. Additional evidence is required. Table 2 shows that the largest dipole moment component for conformer **I** is μ_b, whereas this dipole moment component is practically zero in **II**. Attempts to find a *b*-type spectrum belonging to **I** failed, which is one indication supporting the present assignment. The fact that the theoretical calculations predict that **II** is more stable than **I** is additional evidence pointing in the same direction. Interestingly, the C−C−Se−H *synclinal* conformer of the related compound CH_3CH_2SeH was found experimentally to be 0.8 kJ/mol more stable than the *antiperiplanar* form,[37] which is another indication that aliphatic selenols, such as the title compound, generally prefer a *synclinal* arrangement for the C−C−Se−H chain of atoms.

Comparison of the theoretical (Table 2) and experimental (Table 3) spectroscopic constants is in order. It is seen from these two tables that the experimental values of the *B* and *C* rotational constants are 1.8 and 0.8%, respectively, larger than the B3LYP rotational constants and −0.2 and −1.0%, respectively, smaller in the case of the MP2 rotational constants. The agreement is therefore somewhat better in the case of the MP2 calculations. The discrepancies between the observed and calculated centrifugal distortion constants Δ_J and Δ_{JK} are so large that a comparison is not worthwhile.

The B3LYP calculations predict that the C3−C4 torsional frequency is 80 cm^{-1}. Search for the spectrum of the first excited state of this fundamental mode was made, but an assignment was not obtained, presumably because it is comparatively weak.

Assignment of the $H^{78}SeCH_2CH_2C{\equiv}CH$ Isotopologue of Conformer II. The ^aR-spectrum of conformer **II** of the $H^{78}SeCH_2CH_2C{\equiv}CH$ species was found very close to the prediction. The intensity of this spectrum was roughly half the intensity of the ^{80}Se species, as expected. A total of 118 transitions, which are found in the Supporting Information (Table 2S), were used to obtain the spectroscopic constants presented in Table 3. All the sextic centrifugal distortion constants were kept constant at zero in this case.

Attempts to assign the spectra of the ^{76}Se (9.0%) and ^{82}Se (9.2%) species were made, but these spectra were so weak that a definite assignment could not be achieved.

Assignment of the $H^{80}SeCH_2CH_2C{\equiv}CH$ Isotopologue of Conformer IV. A projection of this rotamer in the *a*−*b* principal axis plane is shown in Figure 2. The rotational constants predicted for the ^{80}Se isotopologue of this conformer (Table 2) indicate that it is a near-prolate rotor with $\kappa \approx -0.91$, with its major dipole moment components along the *a*- and *b*-axes, and a small component along the *c*-axis. This spectrum was also expected to be weak for reasons similar to those given for conformer **II**.

Pileups of ^aR-transitions similar to those observed for **II** were therefore expected in this case as well, because it is a near-prolate rotor. These pileups, which were the key to the assignment in this case as well, were readily identified. $J = 24 \leftarrow 23$ pileup shown in Figure 4 is a typical example. The ^aR-spectrum of this conformer appears to be somewhat stronger than the ^aR-spectrum of **II**.

The *b*-type transitions were assigned next. No *c*-type lines were assigned, presumably because μ_c is small and therefore produces insufficient intensity for these transitions. It was possible to assign *b*-type lines up to $J = 80$. Transitions involving even higher values of the principal quantum number *J* were searched for but not found, presumably because of insufficient intensities. A total of 468 transitions, which are shown in Table 3S in the Supporting Information, were used to determine the spectroscopic constants listed in Table 4. It was necessary to use two sextic centrifugal distortion constants (Φ_{JK} and ϕ_J) to obtain a fit with a favorable root-mean-square deviation.

The conformers **III**, **IV**, and **V** are calculated to have rather similar rotational constants (Table 2), and a definite conformer assignment cannot be made unless additional information is available. Fortunately, the calculated dipole moment components shown in the same table support the present assignment. Conformer **III** has a very small μ_a according to these calculations, which is in disagreement with the observations. Conformer **V** has much larger μ_b than μ_a, which is also in disagreement with the observations. The fact that μ_a and μ_b are predicted to be of equal magnitude for **IV** agrees with the observed intensities in the present case. Moreover, both **III** and **V** are calculated to be less stable than **IV** by several kilojoules per mole (Table 2), which is also an indication supporting the present conformer assignment.

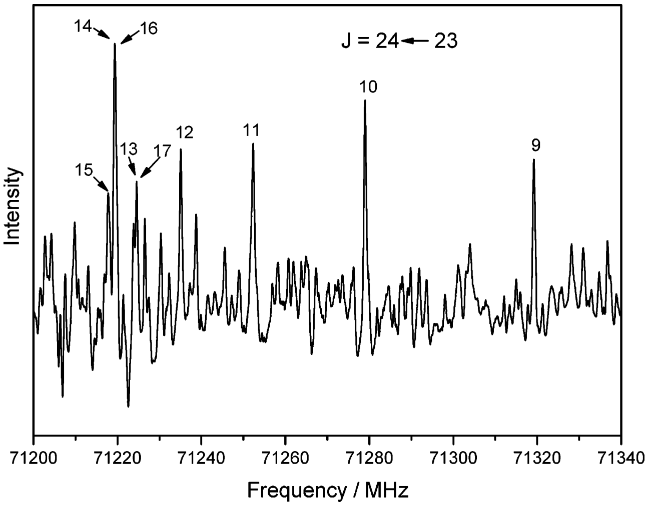


Figure 4. This portion of the MW spectrum of 3-butyne-1-selenol shows the *a*-type $J = 24 \leftarrow 23$ transition of the ground vibrational state of the $H^{80}SeCH_2CH_2C{\equiv}CH$ isotopologue of conformer **IV**. The values of the coalescing K_{-1} lines are shown above each assigned lines. The $K_{-1} = 14$ and 16 lines and the $K_{-1} = 13$ and 17 lines overlap. The spectrum was recorded applying a Stark-modulation field strength of approximately 320 V/cm.

The experimental rotational constants *A*, *B*, and *C* in Table 4 are larger by 3.5, 5.2, and 3.7%, respectively, than their B3LYP counterparts in Table 2. The corresponding differences are 1.0, −2.1, and −1.6%, respectively, in the MP2 case. It is likely that this implies that the MP2 structure is somewhat more accurate than the B3LYP structure. However, the quartic centrifugal distortion constants (Table 2) obtained in the B3LYP calculations generally agree better than the MP2 constants with the experimental values (Table 4).

Vibrationally Excited State of the $H^{80}SeCH_2CH_2C{\equiv}CH$ Isotopologue of Conformer IV. The MW spectrum of the first excited state of the torsion of the ^{80}Se species about the C3−C4 bond of this rotamer was assigned. The spectroscopic constants of this state obtained from 328 transitions, which are shown in Table 4S in the Supporting Information, are listed in Table 4. Maximum value of *J* was 62 in this case.

Relative intensity measurements performed as described elsewhere[38] yielded 78(25) cm^{-1} for this fundamental vibration. The uncorrected B3LYP value is 83 cm^{-1}, and the uncorrected MP2 result is 94 cm^{-1} for this vibration.

Assignment of the $H^{78}SeCH_2CH_2C{\equiv}CH$ Isotopologue of Conformer IV. The assignment of the spectrum of the ^{78}Se isotopologue was straightforward. The spectrum consisting of 186 transitions with $J_{max} = 50$ is listed in Table 5S in the Supporting Information, and the spectroscopic constants are given in Table 4.

Attempts to assign the spectra of the ^{76}Se (9.0%) and ^{82}Se (9.2%) species were made, but these spectra were again found to be so weak that a detailed assignment could not be achieved.

Internal Energy Difference between II and IV. The internal energy difference between **II** and **IV** has been derived using a

TABLE 4: Experimental Spectroscopic Constants[a] of the $H^{80}SeCH_2CH_2C{\equiv}CH$ and $H^{78}SeCH_2CH_2C{\equiv}CH$ Isotopologues of Conformer IV of 3-Butyne-1-selenol

species: vib state[e]:	$H^{80}SeCH_2CH_2C{\equiv}CH$[b] ground	$H^{80}SeCH_2CH_2C{\equiv}CH$[c] C3−C4 torsion[f]	$H^{78}SeCH_2CH_2C{\equiv}CH$[d] ground
A (MHz)	6715.3765(30)	6780.2621(49)	6723.5907(65)
B (MHz)	1603.26313(45)	1595.8765(10)	1616.0758(13)
C (MHz)	1357.48957(74)	1352.53715(97)	1366.9875(13)
Δ_J (kHz)	1.00526(67)	1.00451(91)	1.0233(11)
Δ_{JK} (kHz)	−8.6140(23)	−8.9812(38)	−8.7223(75)
Δ_K (kHz)	32.070(39)	35.019(45)	32.441(68)
δ_J (kHz)	0.257878(47)	0.25663(13)	0.262907(93)
δ_K (kHz)	2.4649(22)	2.6042(30)	2.4739(63)
Φ_{JK} (Hz)	0.02456(46)	0.0243(12)	0.0225(31)
ϕ_J[g] (Hz)	0.0001129(66)	0.000100(29)	h
rms[i]	1.2022	1.2535	1.1837
no. of transitions	468	328	186

[a] A-reduction I^r representation.[31] Uncertainties represent one standard deviation. [b] Full spectrum in Table 3S in the Supporting Information. [c] Full spectrum in Table 4S in the Supporting Information. [d] Full spectrum in Table 5S in the Supporting Information. [e] Vibrational state. [f] First excited state of the torsion about the C3−C4 bond. [g] Further sextic distortion constants preset at zero. [h] Preset at zero. [i] Root-mean-square deviation.

variant of eq 3 of Esbitt and Wilson.[38] According to Wilson,[39] the internal energy difference is given by

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

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

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

where S is the peak signal amplitude of the radiation-unsaturated line, g is the degeneracy other than the rotational degeneracy, which is $2J + 1$, ν is the frequency of the transition, μ is the principal axis dipole moment component, l is the radiation wave length in the Stark cell,[40] $\Delta\nu$ is the line breadth at half-height, λ is the line strength, and J is the principal rotational quantum number.

The intensities of carefully selected ^aR-lines of the $J = 24 \leftarrow 23$ transition of **IV** were compared with ^aR-lines of the $J = 36 \leftarrow 35$ transition of **II**. Similar comparisons were made for the $J = 22 \leftarrow 21$ of **IV** and $J = 33 \leftarrow 31$ of **II**. The intensity comparison was performed as described by Esbitt and Wilson.[38] The statistical weight (g) of each rotamer was assumed to be the same (2), and the radiation wavelengths (l) were assumed to be identical. The B3LYP μ_a dipole moment components of the two forms (Table 2) were employed, because it was not possible to determine the dipole moment experimentally, since the intensity is so low.

The internal energy difference, $E_{\mathbf{II}} - E_{\mathbf{IV}}$, obtained this way varied between −0.2 and 0.7 kJ/mol in the four comparisons that were performed. The average value was found to be $E_{\mathbf{II}} - E_{\mathbf{IV}} = 0.2$ kJ/mol. There are several sources of errors in this procedure. One standard deviation has been conservatively estimated to be ±0.5 kJ/mol by taking into account plausible uncertainties of the many parameters of eq 2.

The fact that **IV** tends to be 0.2(5) kJ/mol more stable than the **II** form should be compared with the theoretical results. The MP2 prediction of this energy difference (Table 2) is 1.6 kJ/mol, whereas the B3LYP method yields −2.2 kJ/mol. The MP2 prediction is therefore closer to the experimental value than the B3LYP result.

Discussion

Of the two conformers of 3-butyne-1-selenol detected by MW spectroscopy, the potential for intramolecular hydrogen bonding exists in **IV** only. The MP2 structure of **IV** appears to be more accurate than the B3LYP structure, as noted above, and is therefore used to discuss the interaction between the H atom of the selenol group and the π electrons of the triple bond.

The MP2 nonbonded distances (Table 1) between H11 and C1 and between H11 and C2 are 294.6 and 273.2 pm, respectively. The nonbonded distance between H1 and the midpoint of the C1≡C2 triple bond is 282.8 pm (not given in Table 1). These values should be compared to the sum, 290 pm, of the van der Waals radii of the half thickness of aromatic carbon (170 pm) and hydrogen (120 pm).[41] This apparent reduction in the distance between the H11 and the π electrons, relative to their sum of the van der Waals radii, suggests that conformer **IV** is, indeed, stabilized by a weak intramolecular H bond. This weak interaction does not manifest itself in the harmonic B3LYP and MP2 Se−H stretching vibration, which varies little between the five rotamers.

The fact that $HSeCH_2CH_2C{\equiv}CH$ prefers the H-bonded conformer as its lowest energy form is similar to the conformational behavior of the alcohol ($HOCH_2CH_2C{\equiv}CH$),[4,5] thiol ($HSCH_2CH_2C{\equiv}CH$),[6] and amine ($H_2NCH_2CH_2C{\equiv}CH$)[7] analogues. The strongest H bond in these compounds is presumably found in $HOCH_2CH_2C{\equiv}CH$, since the electronegativity difference between O and H is 1.24,[41] which is an indication that the O−H bond is very polar. The second strongest H bond interaction is presumably found in the corresponding amine, because the electronegativity difference between N and H is 0.84.[41] Interestingly, no non-hydrogen-bonded rotamers have been assigned for these two molecules, presumably because their energies are high relative to the energies of the H-bonded conformers.

The electronegativity difference is 0.38 between S and H,[41] compared to 0.35 between Se and H.[41] The H bond strength is therefore expected to be weaker in the thiol and selenol compared to its strength in $HOCH_2CH_2C{\equiv}CH$ and $H_2NCH_2CH_2C{\equiv}CH$. Conformers similar to **II** and **IV** were assigned for $HSCH_2CH_2C{\equiv}CH$, with the non-hydrogen-bonded form being higher in energy by 1.7(4) kJ/mol,[6] compared to 0.2(5) kJ/mol found in the present study of $HSeCH_2CH_2C{\equiv}CH$, which appears to have the weakest H bond of these four 3-butynes.

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Supporting Information Available: The microwave spectra of conformers **II** and **IV**. This material is available free of charge via the Internet at http://pubs.acs.org.

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