

3-Buteneselenol—The First Example of a Selenol with an Intramolecular Hydrogen Bond as Studied by Microwave Spectroscopy and Quantum Chemical Calculations

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The microwave spectrum of 3-buteneselenol ($\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{SeH}$) has been investigated in the 24–62 GHz spectral range by Stark microwave spectroscopy and by Fourier transform microwave spectroscopy in the 6–20 GHz region. High-level quantum chemical calculations carried out for 14 conformers predict that their energies fall within a narrow range of less than 7 kJ/mol. The most stable conformer was predicted to have an intramolecular hydrogen bond formed between the hydrogen atom of the selenol group and the double bond. The microwave spectra of the three most stable conformers were assigned. One of these rotamers has an internal hydrogen bond, whereas the two others are without this interaction. It was found by relative intensity measurements that the hydrogen-bonded conformer is 1.6(7) and 1.9(5) kJ/mol, respectively, more stable than the two other rotamers. As far as we know, this is the first example of a gas-phase study demonstrating that a selenol indeed participates in intramolecular hydrogen bonding.

Introduction

The role played by intramolecular hydrogen (H) bonding for the conformational composition of gaseous 3-butenes have been investigated in the past in $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{OH}$,^{1–3} $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{SH}$,^{4,5} and $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{NH}_2$.⁶

Two H-bonded species were found for 3-buten-1-ol ($\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{OH}$) in the electron-diffraction study,¹ whereas one H-bonded species was observed in the microwave (MW) investigations.^{2,3} In the corresponding thiol ($\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{SH}$), one conformer stabilized by this interaction was identified in the MW spectrum together with two other rotamers without internal H bonds.^{4,5} The H-bonded rotamer was about 3 kJ/mol more stable than each of the two other forms. Interestingly, the amino group acts as an “acid” even in amines such as $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{NH}_2$.⁶ Four conformers were assigned in this case, two with and two without H bonds. The two H-bonded forms are the most stable ones in this case too.

The present study of the selenium analogue, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{SeH}$, is an extension of the studies mentioned above. Very few investigations of the conformational properties of gaseous selenols have been made presumably owing to their toxicity, obnoxious smells, and instability. The literature on the ability of selenols to participate in intramolecular H bonding is even scantier. No studies of gaseous compounds with this interaction have to the best of our knowledge been reported previously.

Rotation around the two C–C single bonds and the C–Se bond may result in a large number of conformers of 3-buten-

eselenol. A total of 14 conformers that can be identified by spectroscopy can be envisaged for the title compound. These forms are drawn in Figure 1, where they have been given Roman numbers for reference. Atom numbering is indicated on Conformer I.

Three of these rotamers, VII, II, and XIII, contain what could be termed weak intramolecular H bonds. Conditions for forming an internal H bond are much better in VII than in II or XIII because the H atom here is closer to the π electrons of the double bond than in the two other cases. H-bonded conformers corresponding to VII were indeed the ones assigned for $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{OH}$ ^{2,3} and $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2\text{SH}$ ^{4,5} by MW spectroscopy, whereas two similar H-bonded rotamers were seen for 3-butenamine.⁶

The conformations of 3-buteneselenol shown in Figure 1 were expected to have energies that do not vary widely resulting in a mixture of rotamers where several of them would be present in relatively large amounts. Moreover, among the six isotopes of selenium, there are five with concentrations higher than 7% of the total (⁸⁰Se (49.6%), ⁷⁸Se (23.8%), ⁷⁶Se (9.4%), ⁸²Se (8.7%), and ⁷⁷Se (7.6%)). Each isotopomer will have an independent MW spectrum superimposed on the spectra of the other isotopomers. An experimental method with a superior resolution is thus desirable to deal with such a complicated situation. Microwave spectroscopy meets this requirement and this is the reason for our choice of this spectroscopic method. In addition, the conformational properties have been explored by high-level quantum chemical calculations because such calculations are now able to predict rather accurate molecular properties even for compounds containing atoms with as many electrons as selenium (34) thus complementing the MW study in an ideal manner.

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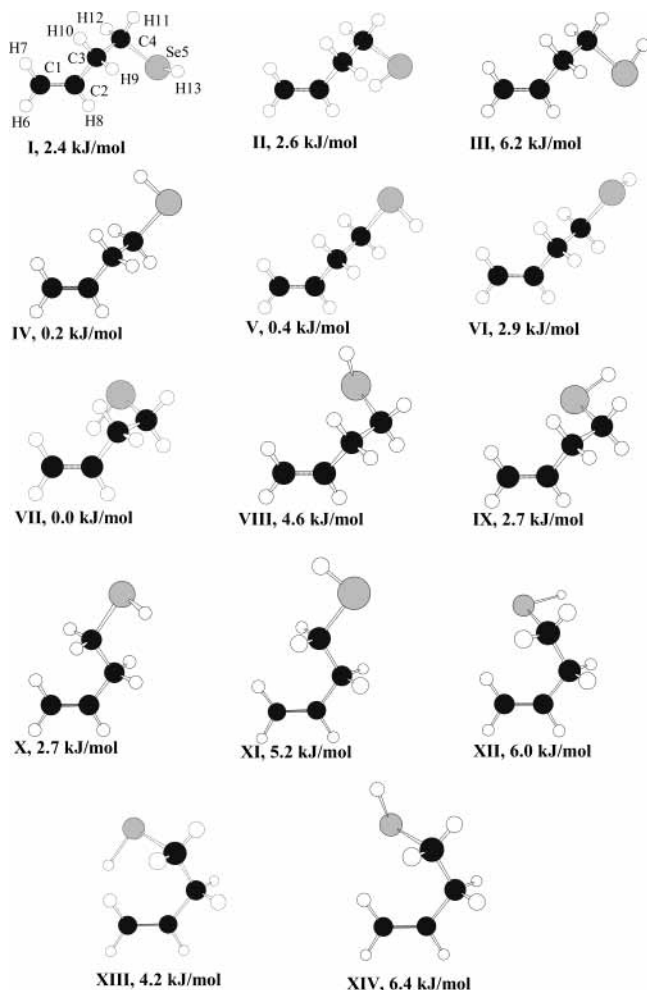
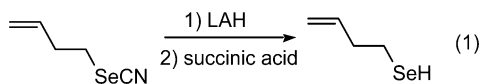


Figure 1. Fourteen possible conformers of 3-buteneselenol. Theoretical G2MP2 relative energies are indicated (see text). Conformers VII, IV, and V were assigned in this work. VII is stabilized by an intramolecular hydrogen bond.

Experimental Section

Synthesis. *Caution:* The 3-buteneselenol is potentially highly toxic. All reactions and handling should be carried out in a well-ventilated hood.



3-Buteneselenol has been prepared starting from selenocyanic acid, 3-butene ester by modification of the approach previously reported (eq 1).⁷ The apparatus already described for the reduction of dibromopropargylphosphine was used.⁸ A 50-mL two-necked flask containing succinic acid (10 mmol) diluted in tetraglyme (10 mL) was fitted on a vacuum line, immersed in a 0 °C cold bath and degassed. In a 25-mL two-necked flask equipped with a stirring bar and a nitrogen inlet, lithium aluminum hydride (100 mg, 2.4 mmol) and tetraglyme (10 mL) were introduced. The flask was immersed in a bath cooled at 0 °C and the selenocyanic acid, 3-butene ester (322 mg, 2 mmol) diluted in tetraglyme (1 mL) was slowly added. After 10 min of stirring, this solution was then slowly added (10 min) with a syringe through the septum in the flask containing the succinic acid. During and after the addition, 3-buteneselenol was distilled off in vacuo (10^{-1} mbar) from the reaction mixture. A first cold trap (−35 °C) removed selectively the less volatile products

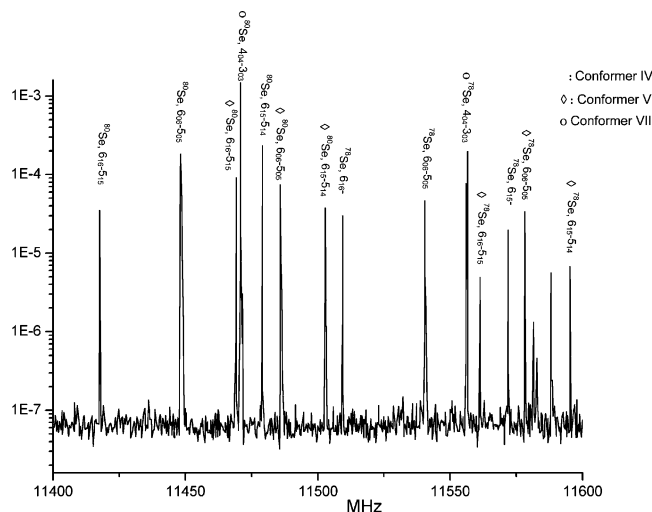


Figure 2. A portion of the Fourier transform spectrum. The intensity scale is arbitrary.

and 3-buteneselenol was selectively condensed in a second trap cooled at −80 °C. At the end of the reaction, this second trap was disconnected from the vacuum line by stopcocks and kept at low temperature (<−30 °C) before analysis. This cell was fitted onto the microwave spectrometers to record the MW spectrum. Yield: 87% bp \approx −40 °C (0.1 mmHg). No decomposition was observed after several weeks in a freezer (−30 °C).

Stark Spectrometer Experiment. The MW spectrum was studied using the Oslo Stark spectrometer, which is described briefly in ref 9. A 3-m Stark cell made of brass was utilized. Radio frequency microwave double resonance (RFMWDR) experiments were carried out as described in ref 10 using the equipment mentioned in ref 6. The 24–62 GHz spectral regions were investigated with the cell cooled to about −30 °C. Lower temperatures, which would have increased the intensity of the spectrum, could not be employed owing to insufficient vapor pressure of the compound. The pressure was a few Pa when the spectrum was recorded and stored electronically using the program written by Waal.¹¹ The accuracy of the spectral measurements was better than ± 0.10 MHz and the maximum resolution was about 0.4 MHz. The compound showed no signs of decomposition in the brass cell even at room temperature.

Fourier Transform Spectrometer Experiments. Rotational spectra in the 6–20 GHz spectral range were recorded with the Lille microwave Fourier transform (MWFT) spectrometer.¹² Neon was used as the carrier gas. A gas mixture of 3 mbar of 3-buteneselenol and 1 bar of neon was prepared and then expanded into the vacuum tank through a pulsed nozzle to create a supersonic beam parallel to the optical axis of the Fabry–Perot cavity.

To facilitate assignments of the different isotopomers and conformers of the molecule, we carried out large spectral region surveys using the fast scan mode facilities of the spectrometer. In this operating mode, around 10 free induction decays were averaged and Fourier transformed at a repetition rate of 1.5 Hz. Two data are then collected, namely, the maximum intensity of the spectrum and the corresponding frequency. This operation is then automatically repeated every 0.4 MHz to cover step by step the whole desired frequency region. An example of such a collection of data is given in Figure 2. Each molecular transition can be reinvestigated with a higher frequency resolution (2.4 kHz per point). The central frequencies of the lines are determined by averaging the frequencies of the two Doppler

TABLE 1: Predicted Energy Differences,^a Dihedral Angles, and Rotational Constants^b of the Conformers of ⁸⁰Se Isotopomer of 3-Buteneselenol

conf.	<i>E</i> ^a	dihedral angle (deg)			rotational constants(MHz)		
		C ₁ C ₂ C ₃ C ₄	C ₂ C ₃ C ₄ Se ₅	C ₃ C ₄ Se ₅ H ₁₃	A	B	C
I	2.4	-120	-65	-70	8827	1225	1135
II	2.6	-115	-67	75	8820	1226	1133
III	6.2	-119	-67	-175	8760	1258	1158
IV	0.2	-116	-176	-65	17638	939	930
V	0.4	-117	179	66	16999	942	936
VI	2.9	-118	-178	-179	17256	958	945
VII	0.0	-122	71	-57	6252	1475	1267
VIII	4.7	-124	69	72	6253	1450	1258
IX	2.8	-124	62	159	5946	1596	1336
X	2.8	0	-177	-67	14303	1033	981
XI	5.3	0	-180	-180	14546	1049	991
XII	6.0	-5	-73	-84	6259	1559	1362
XIII	4.2	-11	-76	59	6415	1515	1340
XIV	6.4	-5	-68	-146	6038	1671	1430

^a Relative energy (kJ/mol) at the G2MP2 level. ^b B3LYP/6-311++G** structure.

components after transformation of 4000 data points time domain signal, leading to a resolution of 2.4 kHz in the spectrum. The accuracy of frequency measurements is estimated to be better than 3 kHz.

Results and Discussion

Quantum Chemical Calculations. All calculations were performed with the Gaussian 98 suite of programs.¹³ The first predictions of the rotational constants of the ⁸⁰Se isotopomer of the 14 conformers shown in Figure 1 were made using density functional theory with the hybrid functional B3LYP (Becke's three parameter functional employing the Lee, Yang, and Parr correlation functional).¹⁴ The 6-311++G** basis set as implemented in Gaussian 98 was used in these calculations. The structures of the rotamers were fully optimized. The C₁=C₂-C₃-C₄, C₂-C₃-C₄-Se₅, and C₃-C₄-Se₅-H₁₃ dihedral angles determine the essential conformational features of the 14 forms. These dihedral angles and the predicted rotational constants obtained in the B3LYP/6-311++G** calculations are collected in Table 1.

The structures of these 14 forms were next used as the starting point to calculate their *relative* energies using the G2MP2 procedure.¹⁵ The G2MP2 method is not expected to be highly accurate in this case because of the presence of the selenium atom. However, the errors are likely to be mainly systematic. Thus, the relative energies of the conformers should be rather reliable. Conformer VII was predicted to be the most stable one in the G2MP2 calculations. It is convenient to assign a relative energy of 0 kJ/mol to this form. The G2MP2 energies relative to VII of the 13 other rotamers are listed in Table 1 and indicated on Figure 1 as well.

Interestingly, conformer VII which has the best conditions for forming an internal H bond, is predicted to be the favored form of the molecule, but the energy differences are not large (up to 6.4 kJ/mol; Table 1 and Figure 1). Moreover, rotamers IV and V are predicted to have marginally higher energies than VII (0.2 and 0.4 kJ/mol, respectively). IV and V are the counterparts of the high-energy forms of the corresponding thiol^{4,5} and amine,⁶ which seems plausible.

The quantum chemical calculations made above indicated that conformers IV, V, and VII would be the ones whose MW spectra one might have the best hope to assign. The B3LYP/6-311++G** calculations (Table 1) were not expected to be very accurate owing to the selenium atom with its 34 electrons. Calculations at a higher level of theory would be desirable to

TABLE 2: Structure of the Three Most Stable Conformers of 3-Buteneselenol at the MP2/6-311++G(3df,2pd) Level of Theory (Distances in pm and Angles in Degree)

conformer:	IV	V	VII
<i>r</i> (C ₁ =C ₂)	133.5	133.5	133.5
<i>r</i> (C ₁ -H ₆)	108.1	108.1	108.1
<i>r</i> (C ₁ -H ₇)	108.3	108.3	108.2
<i>r</i> (C ₂ -C ₃)	149.7	149.7	149.4
<i>r</i> (C ₂ -H ₈)	108.6	108.6	108.7
<i>r</i> (C ₃ -C ₄)	152.6	152.6	152.9
<i>r</i> (C ₃ -H ₉)	109.2	109.3	109.4
<i>r</i> (C ₃ -H ₁₀)	109.2	109.1	109.1
<i>r</i> (C ₄ -Se ₅)	195.4	195.4	195.3
<i>r</i> (C ₄ -H ₁₁)	108.8	109.0	108.9
<i>r</i> (C ₄ -H ₁₂)	109.1	108.9	109.0
<i>r</i> (Se ₅ -H ₁₃)	146.2	146.2	146.2
∠(C ₂ C ₁ H ₆)	121.47	121.46	121.37
∠(C ₂ C ₁ H ₇)	120.93	120.92	120.88
∠(C ₁ C ₂ C ₃)	124.25	124.11	124.46
∠(C ₁ C ₂ H ₈)	119.10	119.09	119.09
∠(C ₂ C ₃ C ₄)	110.59	110.63	112.04
∠(C ₂ C ₃ H ₉)	110.59	110.12	109.26
∠(C ₂ C ₃ H ₁₀)	109.87	110.30	110.20
∠(C ₃ C ₄ Se ₅)	113.59	113.58	113.68
∠(C ₃ C ₄ H ₁₁)	110.99	110.39	111.01
∠(C ₃ C ₄ H ₁₂)	110.82	111.43	110.66
∠(C ₄ C ₅ H ₁₃)	94.42	94.50	94.26
τ(H ₆ C ₁ C ₂ C ₃)	178.7	178.7	-180.8
τ(C ₁ C ₂ C ₃ C ₄)	-112.8	-113.0	-115.1
τ(C ₁ C ₂ C ₃ H ₁₀)	8.3	8.4	7.3
τ(C ₂ C ₃ C ₄ Se ₅)	-176.9	179.4	69.4
τ(C ₂ C ₃ C ₄ H ₁₁)	60.0	62.2	-53.7
τ(C ₂ C ₃ C ₄ H ₁₂)	-59.7	-57.5	-173.6
τ(C ₃ C ₄ Se ₅ H ₁₃)	-62.6	63.1	-53.2

have the best predictions of the rotational constants. Such calculations were for economic reasons carried out only for the three forms (IV, V, and VII). Their dipole moment components and final structures were calculated using the 6-311++G(3df,2pd) basis set. Electron correlation was included using the second-order Møller-Plesset (MP2) perturbation theory.¹⁶ The structures predicted in these calculations are given in Table 2. The rotational constants and dipole moments are listed in Table 3.

Not surprisingly, the MP2 rotational constants (Table 3) vary several percent from the B3LYP values (Table 1), largely because the C₄-Se₅ distance is calculated to be about 0.04 Å shorter in the former procedure.

Centrifugal distortion is important in this compound. The harmonic force fields and the centrifugal distortion constants of these three forms were therefore calculated at the B3LYP/

TABLE 3: Calculated Rotational Constants (MHz),^a Quartic Centrifugal Distortion Constants (kHz),^b and Dipole Moment (D)^a of the ⁸⁰Se Isotopomer of 3-Buteneselenol

	IV ^c	% diff. ^d	V ^e	% diff. ^d	VII ^f	% diff. ^d
A	17177.1	1.4	16765.6	3.8	6038.9	1.1
B	970.2	-1.2	970.6	-1.1	1618.9	-3.4
C	961.6	-1.3	967.3	-1.4	1358.9	-2.6
Δ_J	0.0908	10.4	0.0989	7.6	0.961	7.1
Δ_{JK}	-6.22	8.8	-7.16	5.8	-6.61	7.1
Δ_K	352.9		388.5		24.5	-27.7
δ_J	-0.0025		-0.0029		0.229	10.2
δ_K	4.82		5.90		2.50	3.1
μ_a	-1.29		1.21		-1.27	
μ_b	0.069		0.578		0.881	
μ_c	-0.244		0.256		0.257	
μ_t	1.31		1.55		1.56	

^a MP2/6-311++G(3df,2pd) level. ^b B3LYP/6-311++G(3df,2pd) level. ^c Conformer IV. ^d Percent difference between experimental (Table 3) and theoretical parameter. ^e Conformer V. ^f Conformer VII.

6-311G++(3df,2dp) level of theory with the results shown in Table 3. This table also contains some comparisons with experimental findings that will be discussed below.

Stark Spectrum and Assignments. The five isotopes of selenium and the presumed presence of several conformers each with well-populated vibrationally excited states should lead to a relatively weak, very rich, and extremely complicated Stark spectrum. This was indeed found. Absorption lines are seen every few MHz throughout the entire MW region.

It is seen in Tables 1 and 3 that the low-energy conformers IV and V are practically symmetrical tops with the largest component of the dipole moment along the *a*-axis. Such spectra may be rather simple because pileups of lines are expected to occur at frequencies given approximately by $(B + C) \times (J + 1)$, where *B* and *C* are the rotational constants and *J* is the rotational quantum number. The fact that most of the transitions of the pileups are modulated at low Stark voltages may simplify such spectra considerably. Survey spectra taken at a Stark voltage of a few V/cm immediately revealed the existence of pileups at frequencies expected for conformers IV and V. However, the pileups had a most complicated fine structure stretching over comparatively large spectral intervals. Overlapping transitions occurred frequently.

It turned out that centrifugal distortion was important with the constant Δ_{JK} playing a key role because it is relatively large. A detailed assignment of the ⁸⁰Se-isotopomer (49.8%) was first obtained for the $J = 17 \leftarrow 16$ transition of Conformer IV after a good starting value of Δ_{JK} had been obtained in the force field calculations (Table 3). The RFMWDR method was employed next to confirm the assignments, which were ultimately extended up to the $J = 33 \leftarrow 32$ transition. Attempts to assign the 78-isotopomer (23.7%) had to be given up owing to the spectral complexities caused by numerous overlapping lines.

The transitions of Conformer V were masked by the spectra of excited states of Conformer IV as well as of the spectra of isotopomers. The assignment of this conformer was therefore only partly achieved by this method. The full assignment is described in the next paragraph.

Unsuccessful RFMWDR experiments were also made to assign other low-energy conformers. Extensive, unsuccessful searches were carried out especially for the H bonded rotamer VII. Its successful assignment was, however, made using Fourier transform spectroscopy to be described next. However, after these last-mentioned assignments had been made, it was no problem identifying transitions belonging to this rotamer in the Stark spectrum.

RFMWDR experiments were also made in attempts to find even further rotamers than the three assigned here, but these searches also failed.

Ultimately, more than 1000 transitions were assigned. However, a very large number of lines remain unaccounted for in the Stark spectrum. A majority of these undoubtedly belong to vibrationally excited states and to isotopomers of forms already assigned. However, the existence in quite large proportions even of further rotamers than the three assigned in this work cannot be completely ruled out.

Fourier Transform Spectrum and Assignments. The Fourier transform spectrum was dense owing to the presence of several conformers and the different isotopomers of selenium. Using the preliminary assignments of the a-type spectra of the two main isotopomers of conformer IV obtained in the Stark studies described above, it was easy to identify the corresponding spectra in the 6–20 GHz region. The b-type spectrum was neither observed in the Stark nor in the MWFT spectra owing to a small μ_b dipole moment component predicted to be only 0.06 D (Table 3). It was therefore not possible to determine an accurate value for the *A* rotational constant of this highly prolate conformer.

Another group of lines falling at higher frequencies and with very similar spectral patterns as that of conformer IV was then assigned to conformer V. The assigned lines were fitted for the two most abundant isotopomers using Pickett's program SPFIT.¹⁷ The spectroscopic constants were determined according to Watson's *A*-reduction in the prolate *I'* representation.¹⁸ It was not possible to determine the Δ_{JK} , δ_J , and δ_K centrifugal distortion constants for IV and V because only a-type R-branch transitions were assigned for these very-near symmetrical top conformers. They were therefore preset at the values obtained in the theoretical calculations (Table 2). The results of the fits are listed in Table 4. The transitions have been weighted according to the inverse square of their experimental uncertainties in the least-squares fit. The full spectra measured in the Fourier and Stark experiments are given in the Supporting Information.

Some lines remained unaccounted for after the assignments of conformers IV and V had been completed. The large intensity of many of these transitions excluded the possibility that they originated from less abundant isotopomers of the conformers IV and V. The G2MP2 method (Table 1) predicted that conformer VII should be the most stable one of all the 14 forms. These relatively strong transitions were soon assigned to VII. Only a-type R-branch lines were identified for this conformer too. The spectroscopic constants of this form are included in Table 3, whereas the spectrum is listed in the Supporting Information.

The percent differences between the experimental (Table 4) and calculated (Table 3) spectroscopic constants are given in Table 3. The largest difference is 3.8%, which can be considered to be satisfactory. The percent differences seen for the centrifugal distortion constants are generally somewhat larger, up to 10.4%. Not surprisingly, the B3LYP/6-311++G** rotational constants (Table 1) are in considerably poorer agreement with the experimentally determined ones than the MP2/6-311++G(3df,2pd) rotational constants are (Table 3).

Energy Differences. Energy differences between conformers can best be made in the static Stark experiment and not the Fourier transform beam experiment where thermal equilibrium is not achieved. The energy differences were determined by relative intensity measurements which were performed observing the precautions of ref 19. The dipole moment components of

TABLE 4: Rotational^a (MHz) and Centrifugal Distortion (kHz) Constants^a of 3-Buteneselenol

	conf. IV		conf. V		conf. VII	
	⁸⁰ Se	⁷⁸ Se	⁸⁰ Se	⁷⁸ Se	⁸⁰ Se	⁷⁸ Se
A	17428(17)	17359(35)	17436.5(22)	17436.5 ^c	6108.6983(34)	6115.8445(27)
B	959.16314(6)	966.83805(15)	959.94488(15)	967.67347(25)	1565.75302(50)	1578.4470(3)
C	948.88701(6)	956.50322(14)	954.37806(15)	962.03122(25)	1325.06580(56)	1334.4873(3)
Δ_J	0.10132(15)	0.10319(20)	0.10699(17)	0.1099(14)	1.0344(15)	1.0529(32)
Δ_{JK}	-6.8282(11)	-6.8819(17)	-7.6036(15)	-7.706(46)	-5.684(10)	-5.786(18)
Δ_K	352.9359 ^b	352.9359 ^c	388.4730 ^b	388.4730 ^c	19.16(70)	19.16 ^c
δ_J	-0.0025 ^b	-0.0025 ^c	-0.0029 ^b	-0.0029 ^c	0.2549(28)	0.2549 ^c
δ_K	4.8232 ^b	4.8232 ^c	5.9037 ^b	5.9037 ^c	2.58(14)	2.58 ^c
N ^d	452	259	323	19 ^e	138	27 ^e
σ^f	89	96	72	3	71	1

^a Watson A-reduction *I'* representation.¹⁸ ^b Fixed at the ab initio value. ^c Fixed at ⁸⁰Se value. ^d Number of fitted lines. ^e Only MWFT lines fitted. ^f Standard deviation in kHz.

the conformers to be compared have to be known. These parameters could not be determined in the Stark experiment owing to insufficient intensities of the spectrum. The theoretical values shown in Table 3 were hence used. It was not straightforward to find suitable lines for intensity comparison not overlapped by others or perturbed by Stark from neighboring transitions. The H bonded conformer VII is 1.9(5) kJ/mol more stable than IV and 1.6(7) kJ/mol more stable than V. The uncertainties are assumed to encompass the systematic uncertainties of the dipole moment as well as baseline uncertainties.

Structure. A full structure of the three identified forms cannot be derived from the rotational constants listed in Table 4. However, it has been pointed out that the MP2 procedure with a large basis set is able to predict accurate equilibrium structures.²⁰ The bond lengths associated with the selenium atom are the most critical parameters to calculate accurately. It is reassuring that the MP2/6-311++G(3df,2pd) procedure appears to represent a satisfactory level of theory as the C₄-Se₅ and Se₅-H₁₃ bond lengths are calculated to be roughly 195.4 and 146.2 pm, respectively, (Table 2) in good agreement with the experimental values of 195.9 and 147.3 pm seen in methyl selenol.²¹ The B3LYP/6-311++G** values of the C₄-Se₅ bond lengths of the 14 conformers were fairly constant and about 199 pm (not given in Table 1), which is in poor agreement with the experimental result found for methyl selenol (195.9 pm).²¹

Some of the structural parameters of the three identified forms warrant comments. It is seen in Table 2 that the C₁=C₂-C₃-C₄ dihedral angles are between -112.8 and -115.1° and that the H₁₀-C₃ bond practically eclipses the double bond in the three forms. C₂-C₃-C₄-Se₅ chain is nearly *antiperiplanar* in conformer IV as well as in V. The fact that $\tau(\text{C}_2\text{C}_3\text{C}_4\text{Se}_5) = 69.4^\circ$ and $\tau(\text{C}_3\text{C}_4\text{Se}_5\text{H}_{13}) = -53.2^\circ$ allows for a maximal internal H bond interaction with the π electrons of the double bond.

The experimentally determined rotational constants and the rotational constants obtained in the quantum chemical calculations are defined differently. However, the differences between them are not expected to be large. Indeed, the rather good agreement between the calculated and observed rotational constants (Tables 3 and 4) is believed not to be fortuitous but reflects that the MP2/6-311++G(3df,2pd) structures in Table 2 are rather close to the true equilibrium structures.

Inspection reveals that there is nothing unexpected about the bond lengths and bond angles of the MP2 structures in Table 2. It is also seen in this table that the dihedral angles take the "canonical" values near 0, ± 60 , ± 120 , or 180° , as one would expect.

Conclusions. Stark and Fourier transform spectroscopy guided by high-level quantum chemical calculations have been

used to assign three rotamers of 3-buteneselenol. The preferred form of this compound is stabilized by an internal H bond formed between the H atom of the selenol group and the π electrons of the double bond. The distances between the H atom of the selenol group and the two carbon atoms of the double bond are calculated from the structure in Table 2 to be about 292 and 275 pm, respectively, compared to the sum of the van der Waals radii of H (120 pm) and aromatic carbon (170 pm), totaling 290 pm.²² The internal H bond is thus quite weak as expected.

The two high-energy conformers IV and V are similar to the high-energy conformers found for the corresponding amine^{4,5} and thiol.⁶ A rough value for the strength of the H bond can be taken to be the energy difference between conformer IV and VII (1.6(7) kJ/mol), and between V and VII (1.9(5) kJ/mol). The corresponding H bond strengths are about 2 kJ/mol in 1-amino-3-butene^{4,5} and about 3 kJ/mol in 3-butenethiol.⁶ The H bonds thus appear to be slightly weaker in the 3-buteneselenol than both in its amino and thiol counterparts.

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Supporting Information Available: The spectra (frequencies of the microwave transitions) of conformers IV, V, and VII are listed in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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