Microwave Spectrum and Intramolecular Hydrogen Bonding of 2-Propene-1-selenol ($H_2C{=}CHCH_2SeH$)

Harald Møllendal,*,[†] Alexey Konovalov,[†] and Jean-Claude Guillemin[‡,§]

Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway, École Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France, and Université européenne de Bretagne

Received: March 12, 2009; Revised Manuscript Received: April 10, 2009

The microwave spectrum of 2-propene-1-selenol, $H_2C{=}CHCH_2SeH$, has been investigated in the 45−80 GHz spectral range at −30 °C. The spectra of six isotopologues of one conformer, which has an anticlinal orientation for the C=C−C−Se chain of atoms and a synclinal conformation for the C−C−Se−H link, were assigned. This conformational preference allows for the formation of an intramolecular hydrogen bond between the hydrogen atom of the selenol group and the π electrons of the double bond. This hydrogen-bonded conformer is at least 3 kJ/mol more stable than any further rotameric form of the molecule. The microwave study has been augmented by quantum chemical calculations at the MP2/6-311++G(3df,3pd) and B3LYP/6-311++G(3df,3pd) levels of theory. These calculations indicate that additional rotamers have higher energies, by ~3−12 kJ/mol, than the identified conformer. The conformational properties and internal hydrogen bonding of $H_2C{=}CHCH_2SeH$ is compared with their counterparts of the corresponding alcohol and thiol.

Introduction

The ability of selenols to form intramolecular hydrogen (H) 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. The next example was cyclopropylmethylselenol ($C_3H_5CH_2SeH$),[2] where the preferred form was found to be stabilized by a weak H bond between the selenol group and the pseudo-π electrons[3] along the edge of the cyclopropyl ring. Recently, 3-butyne-1-selenol ($HSeCH_2CH_2C{\equiv}CH$)[4] was shown to possess an internal H bond formed between the π electrons of the triple bond and the selenol group.

The subject of the current study, namely, 2-propene-1-selenol (allylselenol, $HSeCH_2CH{=}CH_2$), has been chosen to allow a direct comparison of the hydrogen bonding abilities in the analogous alcohol ($HOCH_2CH{=}CH_2$)[5−9] and thiol ($HSCH_2CH{=}CH_2$),[10] both of which are stabilized by intramolecular hydrogen bonding involving the π electrons of the double bond in their lowest-energy conformers. The present investigation of allylselenol represents the first microwave (MW) study of a β,γ-unsaturated selenol.

A model of 2-propene-1-selenol with atom numbering is shown in Figure 1. Rotation about the C2−C6 and C6−Se9 bonds may produce rotational isomerism. A total of five conformers with all-staggered atomic arrangements can be envisaged for this compound, and these rotamers can in principle be identified by MW spectroscopy. These conformers are depicted in Figure 1, and are given Roman numerals for reference. The conformational properties of this compound can conveniently be described by reference to the C1−C2−C6−Se9 and C2−C6−Se9−H10 dihedral angles. The C1−C2−C6−Se9 chain of atoms is anticlinal in conformers **I**, **II**, and **III**, and synperiplanar in the remaining two forms. The C2−C6−Se9−H10 link of atoms is antiperiplanar in **II** and **V**, −synclinal in **I** and **IV**, and +synclinal in **III**. Mirror-image forms, which would have identical MW spectra, exist for all rotamers but **V**, 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 two conformers, namely **I** and **IV**.

The synthesis,[11] the photoelectron spectra,[12] and quantum chemical calculations[12] of the title compound have recently been reported, but no detailed conformational study was undertaken.

A successful investigation of a delicate conformational equilibrium such as the one presented by gaseous 3-propene-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 also represents a continuation of our studies of intramolecular hydrogen bonding, of which 3-butyne-1-selenol ($HSeCH_2CH_2C{\equiv}CH$),[4] 4-pentyn-1-ol ($HO(CH_2)_3C{\equiv}CH$),[13] trifluorothioacetic acid (CF_3COSH),[14] (*Z*)-3-mercapto-2-propenenitrile ($HSCH_2{=}CHC{\equiv}N$),[15] (*Z*)-3-amino-2-propenenitrile ($H_2NCH_2{=}CHC{\equiv}N$),[16] 3-butyne-thiol ($HSCH_2CH_2C{\equiv}CH$),[17] (methylenecyclopropyl)-methanol ($H_2C{=}C_3H_3CH_2OH$),[18] cyclopropylmethylselenol ($C_3H_5CH_2SeH$),[2] 2-chloroacetamide ($CH_2ClCONH_2$),[19] 1,1,1-trifluoro-2-propanol ($CF_3CH(OH)CH_3$),[20] cyclopropylmethylphosphine ($C_3H_5CH_2PH_2$),[21] and 1-fluorocyclopropanecarboxylic acid (C_3H_4FCOOH),[22] are recent examples. Less recent work on gas-phase studies of intramolecular H bonding is reviewed elsewhere.[23,24]

---

* To whom correspondence should be addressed. Tel: +47 2285 5674. Fax: +47 2285 5441. E-mail: harald.mollendal@kjemi.uio.no (H.M.), jean-claude.guillemin@ensc-rennes.fr (J.-C.G.).

[†] University of Oslo.

[‡] École Nationale Supérieure de Chimie de Rennes.

[§] Université européenne de Bretagne.

10.1021/jp902215b CCC: $40.75

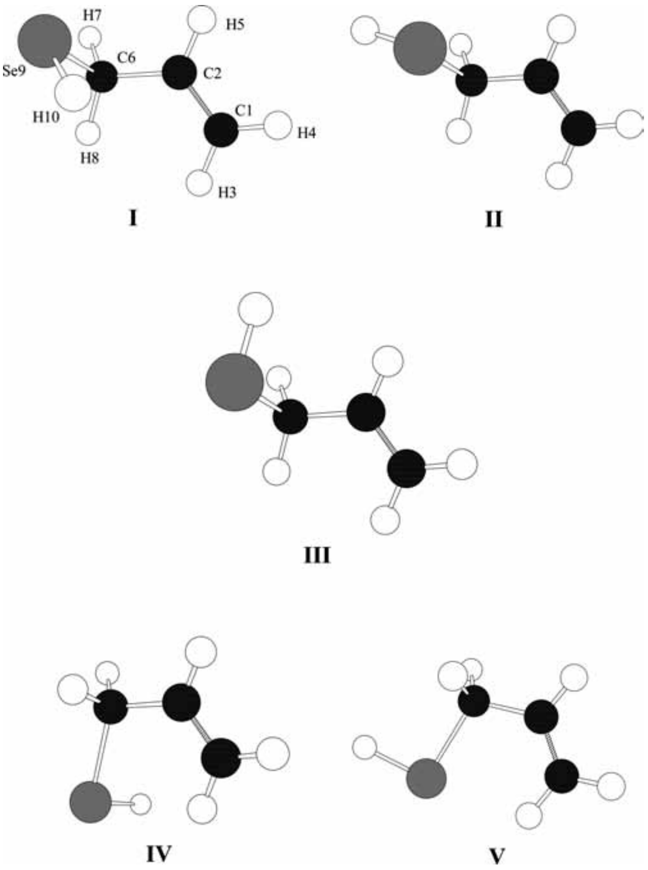
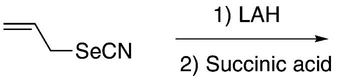


Figure 1. Five possible rotameric forms of $H_2C{=}CHCH_2SeH$. Atom numbering is indicated on conformer **I**, which was assigned and shown to be at least 3 kJ/mol more stable than any other rotamer. Quantum chemical calculations indicate that the remaining forms are ~3−12 kJ/mol less stable than **I**.

Experimental Section

Preparation. 2-Propene-1-selenol has been prepared by reduction of allylselenocyanate.[11,25] The experimental procedure is given in the Supporting Information for the convenience of the reader.



(1)

Caution! Allylselenol and allylselenocyanate are potentially highly toxic compound. All reactions and handling should be carried out in a well-ventilated hood.

Microwave Experiment. The spectrum of 2-propene-1-selenol was recorded in the 45−80 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.[22,26] While the spectrum was recorded, the Stark cell was cooled to approximately −30 °C with solid CO_2, in an attempt to increase the intensity of the spectrum. Radiofrequency microwave double-resonance experiments, similar to those performed by Wodarczyk and Wilson,[27] were also conducted to assign unambiguously particular transitions. 2-Propene-1-selenol is kinetically unstable and was therefore kept at liquid-nitrogen (−196 °C) or dry ice (−78 °C) temperature. The formation of deposits of red elemental selenium in the sample tube was observed when the cell was filled with fresh sample. Decomposition of the compound in the MW cell was also observed. Fresh samples were therefore introduced in the MW cell at regular intervals (~1 h).

Quantum Chemical Methods. A series of quantum-chemical calculations were conducted on 2-propene-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,[28] running on Titan cluster of the University of Oslo.

Geometry optimizations were carried out on the five possible rotameric forms of 2-propene-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).[29] The calculations were performed using the 6-311++G(3df,3pd) basis set,[30] which 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.[31,32]

Results

Quantum Chemical Calculations. The MP2 structures of conformers **I**−**V** obtained in these calculations are shown in Table 1. 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 the MP2 structures are shown in Table 2, together with Watson's *A* reduction quartic centrifugal distortion constants,[33] the components of the dipole moment along the principal inertial axes, and the energy differences relative to the energy of the global minimum conformer, which turned out to be **I**.

Analogous B3LYP calculations were also carried out, but these calculations were extended to include the vibration−rotation constants (the α's)[34] as well, because a MP2 calculation of these constants is too costly. Selected results of these calculations are shown in the Supporting Information Tables 1S and 2S.

The MP2 (Table 2) and B3LYP (Table 2S, Supporting Information) calculations both predict that **I** is the preferred form of the molecule by ~3−12 kJ/mol relative to the four other forms (Figure 1). There are some noteworthy differences in the structures calculated by these two methods, particularly associated with the selenol group. The B3LYP C6−Se9 bond length (Table 2S, Supporting Information) is about 3 pm longer than the MP2 bond length (Table 2), and the B3LYP Se9−H10 bond length is approximately 1 pm longer than its MP2 counterpart. 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.[35] 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.[36] It is seen from Tables 1 and 1S (Supporting Information) 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,[35] 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.[36] These experimental results are not far from the theoretical predictions in Tables 1 and 1S (Supporting Information).

TABLE 1: MP2/6-311++(3df,3pd) Structures of Five Conformers of $H_2{=}CHCH_2SeH$

	conformer				
	I[a]	**II**	**III**	**IV**	**V**
Bond Length (pm)					
C1−C2	**133.6**	133.5	133.5	133.3	133.4
C1−H3	**108.2**	108.2	108.2	108.1	108.2
C1−H4	**108.0**	108.0	108.0	108.0	108.0
C2−H5	**108.4**	108.5	108.5	108.6	108.6
C2−C6	**148.6**	148.9	148.8	149.8	149.4
C6−H7	**109.0**	108.7	108.7	109.2	108.9
C6−H8	**108.7**	108.7	108.9	108.9	108.9
C6−Se9	**196.4**	196.9	196.7	195.0	195.8
Se9−H10	**146.1**	146.2	146.1	146.2	146.0
Angles (deg)					
C2−C1−H3	**121.0**	121.0	121.1	121.3	122.1
C2−C1−H4	**121.3**	121.2	121.3	120.4	120.7
C3−C1−H4	**117.7**	117.7	117.7	118.2	117.3
C1−C2−H5	**119.9**	118.0	119.5	118.7	118.7
C1−C2−C6	**123.4**	119.8	123.9	127.1	126.8
H5−C2−H6	**116.6**	116.6	116.6	114.1	114.5
C2−C6−H7	**111.7**	111.4	112.2	110.1	109.8
C2−C6−H8	**111.8**	111.4	111.2	110.3	109.8
C2−C6−Se9	**111.5**	107.8	112.5	117.1	112.6
H7−C6−H8	**108.8**	110.0	108.6	106.5	108.1
H7−C6−Se9	**103.7**	107.1	107.3	104.1	108.2
H8−C6−Se9	**109.1**	109.1	104.7	108.0	108.2
C6−Se9−H10	**93.7**	95.4	94.3	94.6	93.3
Dihedral Angle (deg)					
H3−C1−C2−H5	**179.3**	179.1	179.6	179.6	180.0
H3−C1−C2−C6	**1.0**	0.9	0.2	−0.7	0.0
H4−C1−C2−H5	**−0.9**	−1.1	−0.2	0.3	0.0
H4−C1−C2−H6	**−179.1**	−179.2	−179.6	180.0	180.0
C1−C2−C6−H7	**−130.0**	−134.2	−125.9	118.1	120.6
C1−C2−C6−H8	**−7.8**	−11.0	−4.0	−124.6	−120.6
C1−C2−C6−Se9	**114.5**	108.6	113.0	−0.5	0.0
H5−C2−C6−H7	**51.7**	47.6	54.7	−62.1	−59.4
H5−C2−C6−H8	**173.9**	170.8	176.5	55.1	59.4
H5−C2−C6−Se9	**−63.8**	−69.5	−66.4	179.2	180.0
C2−C6−Se9−H10	**−55.6**	160.0	66.7	−65.4	180.0
H7−C6−Se9−H10	**−175.9**	40.2	−57.2	172.8	58.4
H8−C6−Se9−H10	**68.3**	−78.8	−172.4	59.8	−58.4

[a] The MW spectrum of this conformer was assigned.

TABLE 2: MP2/6-311++G(3df,3pd) Parameters of Spectroscopic Interest of Five Conformers[a] of $H_2C{=}CHCH_2SeH$

	conformer				
	I[b]	**II**	**III**	**IV**	**V**
Rotational Constants (MHz)					
A	**17680.5**	16546.6	17707.7	12229.6	11967.9
B	**1955.9**	2038.8	1922.8	2465.2	2613.3
C	**1888.3**	1946.3	1880.8	2107.7	2173.6
Quartic Centrifugal Distortion Constants[c] (kHz)					
Δ_J	**0.940**	1.45	0.895	0.835	1.08
Δ_{JK}	**−32.1**	−43.1	−32.7	−3.85	−4.77
Δ_K	**454**	485	514	23.1	22.0
δ_J	**0.118**	0.184	0.0590	0.162	0.233
δ_K	**0.300**	−3.24	−13.4	1.93	2.53
Dipole Moment (10^{-30} C m)					
μ_a	**4.41**	2.80	3.76	4.00	2.54
μ_b	**0.95**	4.27	2.03	2.51	5.02
μ_c	**1.01**	0.22	2.13	1.62	0.0[d]
Energy Difference[e] (kJ/mol)					
ΔE	**0.0**	3.8	3.9	6.4	9.6

[a] Minima on the potential energy hypersurface; see text. [b] The spectrum of this rotamer was assigned. [c] *A* reduction.[33] [d] For symmetry reasons. [e] Relative to conformer **I** and corrected for the zero-point energy. Electronic energy of conformer **I**: −6609 910.32 kJ/mol.

The two methods predict the 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 (Tables 1 and 1S (Supporting Information)). Even larger differences are calculated for the dihedral angles in some cases. It is especially noted that the important C1−C2−C6−Se9 and C2−C6−Se9−H10 dihedral angles are 2.2 and 2.6°, respectively, smaller in conformer **I** 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 C1=C2 double bond in the MP2 than in the B3LYP structure, as can be seen from the nonbonded H10···C1 and H10···C2 distances, whose MP2 values are 348 and 292 pm, respectively, compared to 361 and 302 pm (B3LYP). The MP2 method therefore seems to indicate a stronger H bond interaction than the B3LYP method does.

The quartic centrifugal distortion constants predicted by the two methods varies somewhat (Table 2 and 2S (Supporting Information)). This is not surprising since they depend on the second derivative at the minima of the potential energy hypersurface. The B3LYP dipole moments (same tables) are generally somewhat smaller than their MP2 counterparts, which is typical.

Finally, it should be mentioned that the relative conformer energies previously obtained in MP2 as well as in B3LYP calculations using the cc-pVTZ basis set,[12] are very similar to their counterparts reported in Table 2 and 2S (Supporting Information).

Microwave Spectrum and Assignment of Conformer I of $H_2C{=}CHCH_2{}^{80}SeH$. This rotamer is predicted to be the preferred form of the molecule by several kJ/mol in both the MP2 and B3LYP calculations (Tables 2 and 2S (Supporting Information)).

The intensity of the spectrum depends on the partition function, which governs the population of each quantum state. A comparatively large partition function and consequently a low population of each quantum state is expected at ∼−30 °C. The rotational constants indicate that the rotational part of the partition function is also sizable. The same must be true for the vibrational part because there are five normal vibrations below 600 cm^{-1} (not given in Table 1 or 2) for each rotamer according to the quantum chemical calculations. 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 **I** would have a similar effect on the intensity.

The ^{80}Se isotopologue of **I** is nearly a prolate rotor (Ray's asymmetry parameter[37] $\kappa \approx -0.99$), with μ_a as its major dipole moment component (Table 2). Pile-ups of ^aR-branch transitions separated by approximately $B + C \approx 2.8$ GHz (Table 2) were therefore expected in 45−80 GHz region. Survey spectra revealed series of comparatively strong pile-ups close to their predicted frequencies. Few and weak spectral lines were seen between the pile-ups. Closer inspection revealed that these pile-ups have a complicated fine-structure because they are composed of the spectra of five selenium isotopologues, each with its vibrationally excited states.

The strongest pile-up series was assumed to belong to the parent $H_2C{=}CHCH_2{}^{80}SeH$ species. It was found that pairs of

TABLE 3: Spectroscopic Constants[a] of the Ground and Vibrationally Excited States of $H_2C{=}CHCH_2{}^{80}SeH$

	vibrational state			
	ground	C2−C6 torsion	C6−Se9 torsion	lowest bending
A/MHz	18058(10)	18144[b]	17904[b]	18065[b]
B/MHz	1921.7815(51)	1923.20(12)	1918.69(23)	1918.865(57)
C/MHz	1859.4060(47)	1861.13(12)	1859.99(23)	1856.371(57)
Δ_J/kHz	0.9153(40)	0.8981(38)	0.8972(58)	0.9572(40)
Δ_{JK}/kHz	−34.829(41)	−33.952(20)	−32.697(77)	−36.136(22)
Δ_K/kHz	454[b]	454[b]	454[b]	454[b]
δ_J/kHz	0.118[b]	0.118[b]	0.118[b]	0.118[b]
δ_K/kHz	0.300[b]	0.300[b]	0.300[b]	0.300[b]
Φ_{JK}[c]/Hz	−0.486(65)	0.0[b]	0.0[b]	0.0[b]
n.o.trans.[d]	139	98	60	83
r.m.s.[e]	1.182	1.334	1.492	1.323

[a] *A* reduction I^r representation.[33] Uncertainties represent one standard deviation. [b] Fixed; see text. [c] Further sextic centrifugal distortion constants preset at zero. [d] Number of transitions used in the weighted least-squares fit. [e] Root-mean-square deviation.

${}^aR$-lines with identical $K_{-1} \geq 3$ coalesce, because $\kappa \approx -1$. The high-K_{-1} members of these series are modulated at relatively low Stark fields, which facilitated their assignments. Overlapping of lines was frequently encountered, because several vibrationally excited states occur in these pile-ups. About 150 ${}^aR$-transitions were ultimately assigned for the ground vibrational state of the ^{80}Se-isotopologue. No *b*- or *c*-type lines were found. 139 ${}^aR$-transitions was fitted employing Watson's *A* reduction Hamiltonian with the I^r representation[33] using Sørensen's program Rotfit.[38] The spectrum is shown in Table 6S 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, whose one standard deviation is 10 MHz (Table 3). The quartic centrifugal distortion constants Δ_K, δ_J, and δ_K of this near-prolate rotor could not be determined and were therefore held fixed at the MP2 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 rotational constants of conformers **I**, **II**, and **III** are predicted (Tables 2 and 2S (Supporting Information)) to be so similar that a definite conformer assignment cannot be made on the basis of the rotational constants alone. Additional evidence is required. It is seen from Table 2 that the largest dipole moment component for conformer **I** is $\mu_a \sim 4.4 \times 10^{-30}$ C m. The *a*-axis dipole moment component is also the largest component in the case for **III**. However, rotamers **II** and **III** both have sizable components along the *b*-axis (Table 2 and 2S (Supporting Information)). 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 **I** is more stable than the four other forms is additional evidence pointing in the same direction.

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 *A* rotational constants is 2.1% larger, and both the *B* and *C* rotational constants are 1.8% smaller, than the MP2 rotational constants. Differences of this order of magnitude have to be expected because the experimental and theoretical rotational constants are defined differently. The experimental constants are *effective* parameters, whereas the MP2 constants are calculated from an approximate equilibrium structure. There is also good agreement between the experimental and MP2 centrifugal distortion constants Δ_J and Δ_{JK}.

Vibrationally Excited States of Conformer I of $H_2C{=}CHCH_2{}^{80}SeH$. The MP2 calculations predict that the C2−C6 torsional frequency is 107 cm^{-1}. This spectrum should therefore have about 60% of the intensity of the ground-state spectrum at −40 °C. A spectrum about 60% as strong as the ground state consisting of 98 transitions, was assigned (Table 7S of the Supporting Information). Rough relative intensity measurements yielded ca. 90 cm^{-1} for this vibration. No lines with $K_{-1} < 2$ were identified, presumably due to low intensities, caused by insufficient modulation. It was therefore not possible to determine an accurate value for the *A* rotational constant. The $A =$ 18 144 MHz appearing in Table 3 was kept constant in the least-squares fit. Its value was estimated from the B3LYP vibration−rotation constants (not given in Table 2S, Supporting Information) defined by $\alpha_X = X_0 - X_1$,[34] where X_0 is the rotational constant of the ground state and X_1 is the corresponding constant of the first excited state of a particular vibrational mode. The B3LYP value is $\alpha_A = -86.0$ MHz, which was used to obtain the entry in Table 3 (18 144 MHz). The experimental value obtained from the constants of Table 3 are $\alpha_B = -1.42(13)$ and $\alpha_C = -1.72$ MHz. The corresponding B3LYP values are −4.38 and −2.15 MHz, respectively. There is therefore only order-of-magnitude agreement between theory and experiment in this case.

The spectrum of what is assumed to be the first excited state of the C6−Se9 torsion is given in Table 8S in the Supporting Information. The spectroscopic constants of this state, which were derived in a way analogous to that just described, are tabulated in Table 3. Relative intensity measurements yielded ca. 185 cm^{-1} for this mode. Its B3LYP vibration−rotation constants were +153.90, −4.24, and −4.37 MHz, respectively. The experimental values obtained from the results in Table 3 are $\alpha_B = 3.09(24)$ and $\alpha_C = 0.54$ MHz, which are far from the B3LYP values.

The last vibrationally excited state, whose spectrum is found in Table 9S (Supporting Information), have a frequency of ca. 230 cm^{-1}. The B3LYP vibration−rotation constants were −6.65, +2.21, and +2.28 MHz, respectively. The last two constants can be compared to the values derived from Table 3, namely $\alpha_B = 2.92(8)$ and $\alpha_C = 3.04(8)$ MHz, which is a satisfactory result.

Assignment of Further Isotopologue of I. The ground-state ${}^aR$-spectra of ^{76}Se (9.0%; Table 3S, Supporting Information), ^{77}Se (7.6%; Table 4S, Supporting Information), ^{78}Se (23.5%; Table 5S, Supporting Information), and ^{82}Se (9.2%; Table 10S, Supporting Information) isotopologues were predicted using the structure in Table 1 to obtain shifts in the rotational constants upon substitution of the parent ^{80}Se atom with the other alternatives. These shifts were used to locate the ${}^aR$-spectra, which were readily assigned. The results are presented in Table 4. The *A*-rotational constants had to be estimated in all cases except for the ^{78}Se isotopologue, where several K_{-1} lines were strong enough to be assigned. The value of the *A* rotational constants (18012(16) MHz; Table 4) obtained for this species is less than that obtained for the ^{80}Se isotopologue (18058(10) MHz; Table 3), but the uncertainties are large in these cases and this may explain the apparent inconsistency. Kraitchman's coordinates[39] of the selenium atom calculated from these isotopologues are in good internal agreement and are also in good agreement with coordinates calculated from the MP2 structure, which is additional evidence that the spectrum of **I** has indeed been assigned.

Searches for Further Rotamers. The spectra assigned as described above include all the strongest transitions of the

TABLE 4: Spectroscopic Constants[a] of the Ground State of Isotopologues of $H_2C{=}CHCH_2SeH$

	isotopologue			
	$H_2C{=}CHCH_2{}^{76}SeH$	$H_2C{=}CHCH_2{}^{77}SeH$	$H_2C{=}CHCH_2{}^{78}SeH$	$H_2C{=}CHCH_2{}^{82}SeH$
A/MHz	18076[b]	18072[b]	18012(16)	18049[b]
B/MHz	1948.96(33)	1941.18(27)	1935.4819(81)	1907.806(33)
C/MHz	1886.90(34)	1880.55(28)	1872.3709(64)	1847.937(33)
Δ_J/kHz	0.960(11)	0.9615(98)	0.9253(53)	0.8992(58)
Δ_{JK}[c]/kHz	−35.03(13)	−34.721(81)	−35.324(65)	−34.153(18)
Φ_{JK}[d]/Hz	0.0[b]	0.0[b]	−0.85(10)	0.0[b]
no. trans.[e]	34	32	104	65
rms[f]	1.210	1.127	1.212	1.320

[a] *A* reduction I^r representation.[33] Uncertainties represent one standard deviation. [b] Fixed; see text. [c] Further quartic centrifugal distortion constants preset at the values shown in Table 3. [d] Further sextic centrifugal distortion constants preset at zero. [e] Number of transitions used in the weighted least-squares fit. [f] Root-mean-square deviation.

spectrum. Relatively few and weak lines were observed outside the spectral intervals where the ^aR-spectrum of **I** occurs. This is a strong indication that the H-bonded conformer **I** is the predominating species, since the remaining four conformers shown in Figure 1 should have sizable dipole moments (Table 2) and consequently strong spectra provided they were present in appreciable concentrations. A complication is that the spectrum of conformer **IV** could be affected by tunneling of the selenol group, but the *a*-type lines would not be expected to be perturbed much from a rigid-rotor behavior. These transitions should be the strongest ones of the spectrum of this rotamer, because μ_a is its largest dipole moment component (Tables 2 and 2S (Supporting Information)). The absence of strong lines not attributed to **I** makes us conclude that conformer **I** is more stable than any other rotamer by at least 3 kJ/mol. This is in agreement with the MP2 (Table 2) and B3LYP (Table 2S, Supporting Information) predictions.

Discussion

MP2 structures obtained using a large basis set are generally close to the equilibrium structures.[40] The MP2 structure in Table 1 is therefore used to discuss the interaction between the H atom of the selenol group and the π electrons of the double bond. The MP2 nonbonded distances (Table 1) between H10 and C1 and between H10 and C2 are 348 and 292 pm, respectively. The nonbonded distance between H1 and the midpoint of the C1═C2 triple bond is 314 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 H (120 pm).[41] These nonbonded distances associated with the intramolecular H bond therefore indicate that it is quite weak.

Of the five possible conformers of 2-propene-1-selenol, the potential for intramolecular H bonding exists in **I** and in the hypothetical conformer **IV** only. The theoretical calculations (Tables 2 and 2S (Supporting Information)) indicate that **I** is considerable more stable (∼6−8 kJ/mol) than **IV**. The MP2 nonbonded distances between H10 and C1 is 320 pm, and the distance between H10 and C2 is 314 pm. Moreover, the orientation of the H10 atom with respect to the π bond is more favorable in **I** than in **IV**, because H10 is more directly oriented toward the maximum π electron density above the vinyl group in **I**, whereas H10 approaches this density from the side of the double bond in **IV**. It is possible that these two factors may explain part of the MP2 energy difference between **I** and **IV** (6.4 kJ/mol).

Interestingly, the situation in the corresponding alcohol, $H_2C{=}CHCH_2OH$ is quite different. There is about 50% at 300 K of each of the conformers similar to **I** and **IV**, according to an electron-diffraction investigation.[9] The MW spectrum of conformer **IV** analogue has also been assigned,[7] in addition to the counterpart of rotamer **I**.[5,6] However, in the thiol, $H_2C{=}CHCH_2SH$, a conformer similar to **I** seems to predominate.[10] The situation in the thiol therefore resembles more closely the present findings for the 2-propene-1-selenol rather than for the corresponding alcohol ($H_2C{=}CHCH_2OH$).

The strongest internal H bonds in the $H_2C{=}CHCH_2XH$ series, where X = O, S, or Se, are presumably found in the two forms of the alcohol, since the electronegativity difference between O and H is 1.24,[41] which is an indication that the O−H bond is very polar. Moreover, the nonbonded distance between the H atom of the hydroxyl group and the double bond is also significantly shorter in the two forms of $H_2C{=}CHCH_2OH$ than in the corresponding thiol and selenol, which is favorable for H bonding.

The intramolecular H bond strengths of the thiol and selenol are not expected to differ much for two reasons: The distances between the H atom of the thiol or selenol group in conformers similar to **I** and the π electrons of the double bond do not differ much. In addition, the polarities of the thiol and selenol bonds are quite similar since the electronegativity difference is 0.38 between S and H,[41] compared to 0.35 between Se and H.[41]

Acknowledgment. We thank Anne Horn for her skillful assistance. The Research Council of Norway (Program for Supercomputing) is thanked for a grant of computer time. A.K. thanks The Research Council of Norway for financial assistance through Contract 177540/V30. J.-C.G. acknowledges the Program PCMI (INSU-CNRS) for financial support.

Supporting Information Available: The synthesis, the results of the B3LYP calculations, and the microwave spectra of conformer **I**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Petitprez, D.; Demaison, J.; Wlodarczak, G.; Guillemin, J.-C.; Møllendal, H. *J. Phys. Chem. A* **2004**, *108*, 1403.

(2) Cole, G. C.; Møllendal, H.; Guillemin, J.-C. *J. Phys. Chem. A* **2006**, *110*, 2134.

(3) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.

(4) Møllendal, H.; Mokso, R.; Guillemin, J.-C. *J. Phys. Chem. A* **2008**, *112*, 3053.

(5) Murty, A. N.; Curl, R. F., Jr. *J. Chem. Phys.* **1967**, *46*, 4176.

(6) Badawi, H.; Lorencak, P.; Hillig, K. W., II.; Imachi, M.; Kuczkowski, R. L. *J. Mol. Struct.* **1987**, *162*, 247.

(7) Melandri, S.; Favero, P. G.; Caminati, W. *Chem. Phys. Lett.* **1994**, *223*, 541.

(8) Bakke, J. M.; Schie, A. M.; Skjetne, T. *Acta Chem. Scand., Ser. B* **1986**, *B40*, 703.

(9) Vanhouteghem, F.; Pyckhout, W.; Van Alsenoy, C.; Van den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1986**, *140*, 33.

(10) Sastry, K. V. L. N.; Dass, S. C.; Brooks, W. V. F.; Bhaumik, A. *J. Mol. Spectrosc.* **1969**, *31*, 54.

(11) Riague, E. H.; Guillemin, J.-C. *Organometallics* **2002**, *21*, 68.

(12) Bajor, G.; Veszprémi, T.; Riague, E. H.; Guillemin, J.-C. *Chem.—Eur. J.* **2004**, *10*, 3649.

(13) Møllendal, H.; Dreizler, H.; Sutter, D. H. *J. Phys. Chem. A* **2007**, *111*, 11801.

(14) Møllendal, H. *J. Phys. Chem. A* **2007**, *111*, 1891.

(15) Cole, G. C.; Møllendal, H.; Khater, B.; Guillemin, J.-C. *J. Phys. Chem. A* **2007**, *111*, 1259.

(16) Askeland, E.; Møllendal, H.; Uggerud, E.; Guillemin, J.-C.; Aviles Moreno, J.-R.; Demaison, J.; Huet, T. R. *J. Phys. Chem. A* **2006**, *110*, 12572.

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

(18) Møllendal, H.; Frank, D.; De Meijere, A. *J. Phys. Chem. A* **2006**, *110*, 6054.

(19) Møllendal, H.; Samdal, S. *J. Phys. Chem. A* **2006**, *110*, 2139.

(20) Møllendal, H. *J. Phys. Chem. A* **2005**, *109*, 9488.

(21) Cole, G. C.; Møllendal, H.; Guillemin, J.-C. *J. Phys. Chem. A* **2005**, *109*, 7134.

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

(23) Wilson, E. B.; Smith, Z. *Acc. Chem. Res.* **1987**, *20*, 257.

(24) Møllendal, H. *NATO ASI Ser., Ser. C* **1993**, *410*, 277.

(25) Guram, A. S. *Synlett* **1993**, 259.

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

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

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

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

(30) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(32) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

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

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

(35) Thomas, C. H. *J. Chem. Phys.* **1973**, *59*, 70.

(36) Nakagawa, J.; Okutani, H.; Hayashi, M. *J. Mol. Spectrosc.* **1982**, *94*, 410.

(37) Ray, B. S. *Z. Phys.* **1932**, *78*, 74.

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

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

(40) Helgaker, T.; Gauss, J.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1997**, *106*, 6430.

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

JP902215B