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Microwave Spectrum and Molecular Structure of Etheneselenol

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The rotational spectrum of etheneselenol was investigated in the microwave and millimeter-wave ranges. Two conformers of comparable stability were identified: the syn conformer, which is planar, and the gauche conformer. The experimental study has been coupled with some ab initio calculations, which greatly helped to the identification of the spectra. The etheneselenol-*d* (Se-D) was also investigated and the quadrupole coupling constants of deuterium determined.

Introduction

Vinylic compounds $H_2C{=}CHX$ have been the subject of recent studies in both our groups. The structures of ethenylphosphine $X = PH_2$,[1] ethenylarsine $X = AsH_2$,[2] and ethenylstibine $X = SbH_2$[3] have been investigated by microwave and/or millimeter-wave spectroscopies in Lille while their synthesis elaborated in Rennes. Etheneselenol (or vinylselenol) $H_2C{=}CHSeH$ has been very recently synthesized[4] and the investigation of its microwave and millimeter-wave spectra is the subject of this paper. Two members of the same vinylic series, ethenol $X = OH$ and ethenethiol $X = SH$, have been previously studied.

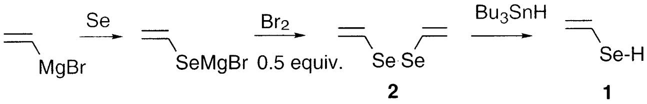
Ethenol was found first in the planar syn conformation[5] and later in the anti conformation,[6] which was also found to be planar. An experimental substitution structure was derived for the syn conformer.[7] The energy difference between the two conformers, calculated at the RHF/6-31G** level, was found to be 8.66 kJ/mol,[5] the syn conformer being the most stable. An experimental value of the energy difference was derived from relative intensities: 4.5 (6) kJ/mol. For both conformers the dipole moment was also determined.[5,6]

Ethenethiol was also found to exist in two conformations. The syn rotamer was studied in the ground and some excited torsional and bending states,[8] including deuterated and doubly deuterated species.[10] This conformation is planar; the dipole moment was determined and some structural information derived. The anti rotamer was also analyzed in the ground and torsional excited states and the dipole moment measured.[9] This anti conformer was also found to be less stable than the syn conformer ($\Delta E = 50$ (25) cm^{-1}). The equilibrium anti conformation shows the H atom of the SeH group out of plane by an angle of 25°. Moreover the analysis of the variations of the rotational constants from the ground state to the torsional excited states ($\upsilon_t = 1, 2, 3$) lead to an experimental determination of the torsional potential. This analysis, first initiated in ref 8, was detailed in ref 10. The conclusion of both analyses is that for the anti conformer the barrier to planarity is lower than the energy of the ground torsional state. From this study the anti conformer can then be considered as planar.

The aim of this work is to extend the study to the next vinylic compound in this series, namely, etheneselenol. The microwave and millimeter-wave spectra were recorded in order to detect both syn and anti conformers and to provide structural information on both conformers, with the help of ab initio calculations.

Experimental Section

The synthesis of etheneselenol is described by the following process, where **1** represents the final product and **2** represents a precursor, namely, diethenyldiselenide.



Diethenyldiselenide (2). Yield ≈63% (crude). To a three-necked flask equipped with a stirring bar, a reflux condenser, and a nitrogen inlet was introduced the vinylmagnesium bromide in THF (0.1 mol, 1 M). Selenium (7.8 g, 0.1 mol) was added portionwise and an exothermic reaction occurred. The mixture was stirred for 30 min at room temperature and then cooled to −30 °C. Bromine (8.0 g, 50 mmol) was added dropwise. The mixture was allowed to warm and stirred at room temperature for 10 min. The solution was then poured into aqueous NH_4Cl solution and the reaction mixture was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$. Compound **1** was always stored as solution (<1 M) and at low temperature (<−20 °C). Attempts to isolate a pure sample or to record the mass spectrum of **2** were unsuccessful. To record spectroscopic data, the solvents of an aliquot of 5 mL were removed in vacuo at low temperature (<−30 °C). A deuterated solvent ($CDCl_3$, 1 mL) was then quickly added and the sample was kept at −20 °C. To prepare a solution in high boiling solvents, tetraglyme (30 mL) was added before to remove the solvents in vacuo at room temperature.

Caution: Etheneselenol is potentially a highly toxic compound and must be used with great care under a well-ventilated hood.

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Etheneselenol (1). The apparatus already described for the reduction of dichlorostibines was used.[11] The flask containing the precursor (2 mmol of **2** in tetraglyme) was fitted on a vacuum line equipped with two traps and the solution was degassed. Bu_3SnH (3 mmol) was then slowly added (30 min) at room temperature with a syringe through the septum. During and after the addition, selenol **1** was distilled off in vacuo (10^{-1} mbar) from the reaction mixture. A cold trap (−70 °C) removed selectively the less volatile products and compound **1** was condensed in a second cold trap (−196 °C) equipped with two stopcocks. At the end of the reaction, the stopcocks were closed, and the trap immersed in a liquid nitrogen bath was connected to the microwave spectrometer.

To prepare the deuterated derivative **1′**, the etheral solution containing the precursor **2** was washed several times with D_2O. After addition of tetraglyme and removal of low boiling solvents in vacuo, the experimental procedure reported above to prepare compound **1** was used with Bu_3SnD as reagent. The product contained still significant amounts of **1**.

The microwave spectra were recorded with the microwave Fourier transform spectrometer in Lille.[12] Several millibars of etheneselenol were mixed with neon, at a total pressure of 1 bar. The mixture was found to be stable during 3−4 h, but a significant decrease of the line intensities was noticed after 1 h. The accuracy of the measured frequencies is about 3−5 kHz.

The millimeter wave spectra were recorded between 150 and 200 GHz with our frequency modulation spectrometer, using a phase-locked backward wave oscillator as a source and a liquid He cooled InSb bolometer as detector. In this case a sample pressure of 20 mTorr of pure etheneselenol was used: the stability of the sample was then around 12 h, in our stainless steel cell. The accuracy of the measured frequencies is about 100 kHz, because the lines were measured in a scanning mode.

Methods of Calculations. All the calculations were performed with the Gaussian 98 suite of programs.[13] The rotational constants were first predicted at the Hartree−Fock level of theory using the 3-21G** basis set as implemented in Gaussian 98. This low level of theory was chosen because there is a large body of documented evidence which shows that it can predict the ground-state rotational constants within a few percents in a few seconds of computer time.

To calculate the harmonic force field and the quartic centrifugal distortion constants, density functional theory with the hybrid functional B3LYP (Becke's three parameter functional employing the Lee, Yang, and Parr correlation functional)[14] was used with the 6-311G(3df,2pd) basis set as implemented in Gaussian 98.

To calculate the dipole moment components and the final structure, electron correlation was included using the second-order Møller−Plesset (MP2) perturbation theory.[15] The correlation consistent triple-ζ valence basis set[16] with the Stuttgart-Dresden-Bonn relativistic core potential (on the Se atom),[17] SDB-cc-pVTZ,[18,19] was chosen because it was found to better reproduce the rotational constants. This, of course, does not prove that this structure is close to the equilibrium structure, but it is known that the MP2/cc-pVTZ C−H internuclear distance is close to the equilibrium one. Furthermore, the MP2/cc-pVTZ C═C internuclear distance is only slightly larger than the equilibrium one (by 0.0014 Å) in $H_2C{=}CH_2$.[20] To estimate the correction for the Se−H internuclear distance, the structure of H_2Se was optimized at the same level of theory, the ab initio Se−H internuclear distance, 1.456 Å, is 0.003 Å shorter than the equilibrium value, 1.459 Å.[21] Unfortunately, it seems difficult to correct the ab initio C−Se internuclear distance because no r_e(C−Se) internuclear distance is accurately known so far. However, the MP2 and B3LYP methods often have an error of opposite sign, the equilibrium value being in between. Assuming that it is true in present case, this gives (in Å): $1.895 \le r_e(C{-}Se) \le 1.909$ for the syn form and $1.902 \le r_e(C{-}Se) \le 1.915$ for the gauche form. The calculated $\angle(HC{=}C)$ angles are expected to be close to the equilibrium values within 0.4°.[22] The accuracy of the $\angle(CSeH)$ angle is probably worse, although it is difficult to estimate it. Finally, the least well-determined parameter is certainly the torsional angle τ(CCSeH) for the gauche form. Using the SDB-cc-pVTZ basis set, the MP2 method gives 151.7°, whereas the B3LYP one gives 164.1°, the true value being probably between these two values. Taking into account the fact that the torsion around the C−Se bond is a large amplitude motion, it would be necessary to use a much larger basis set and probably a higher level method too, to improve the accuracy of the torsional angle. The results are reported in Table 1. As for ethenethiol[10] the dominant relaxation is associated with the CCSe angle, which decreases by 5° degrees going from the syn form to the gauche form.

TABLE 1: MP2/SDB-cc-pVTZ ab Initio Structure of Vinylselenol[a]

	syn	gauche
$r(C_1{=}C_2)$	133.4	133.4
$r(C_2{-}H_{cis})$	108.1	108.1
$r(C_2{-}H_{trans})$	108.1	108.1
$r(C_2{-}Se)$	189.5	190.2
$r(C_1{-}H)$	108.2	108.1
$r(Se{-}H)$	146.0	145.9
$\angle(C_1{=}C_2\text{-}H_{cis})$	122.2	121.9
$\angle(C_1{=}C_2\text{-}H_{trans})$	119.9	120.2
$\angle(H_{cis}C_2H_{trans})$	117.9	118.0
$\angle(C_2{=}C_1\text{-}Se)$	127.2	122.2
$\angle(C_2{=}C_1\text{-}H)$	120.8	121.4
$\angle(Se{-}C_1{-}H)$	112.0	116.2
$\angle(C_1{-}Se{-}H)$	94.3	94.5
$\angle(SeC_1C_2H_{cis})$	0	−4.8
$\angle(HC_1C_2H_{cis})$	180	179.7
$\angle(SeC_1C_2H_{trans})$	180	174.9
$\angle(H_{trans}C_2C_1H)$	0	−0.5
$\angle(C_2C_1SeH)$	0	151.7
$\angle(HC_1SeH)$	180	−32.6
A, MHz	47397.5	45241.6
B, MHz	3971.4	4049.7
C, MHz	3664.4	3742.1
μ_a, D	0.25	0.74
μ_b, D	0.88	0.80
μ_c, D	0	0.20
μ_t, D	0.91	1.11

[a] Distances in picometers and angles in degrees; molecular constants calculated for the ^{80}Se species.

The energy difference between the stable conformers was estimated by the Gaussian-2 (G2) theory.[23] The syn conformer was found more stable than the gauche conformer by $\Delta E = 0.36$ kcal/mol (126 cm^{-1}). It has to be noted that at the G3 level of theory,[24] the energy difference between the syn and gauche conformers of ethenethiol is calculated to be 0.35 kcal/mol, which confirms the great similarity between ethenethiol and etheneselenol (the G3 theory is significantly more accurate than the G2 theory, but it may only be used for molecules containing first- and second-row atoms, which excludes etheneselenol). The potential function for internal rotation around the C−Se bond has been calculated at the B3LYP/6-311(3df,-2pd) level of theory with complete geometry optimization. The height of the barrier between the syn and the gauche rotamers is about 740 cm^{-1} (with $\tau(CCSeH) = 75°$). The anti conformation is subject to a double minimum potential with a very small

TABLE 2: Observed Microwave Frequencies for the Various Isotopomers of the Two Conformers of Etheneselenol (in MHz)

	^{82}Se	^{80}Se	^{78}Se	^{77}Se	^{76}Se	^{74}Se
			syn Form			
1_{01}-0_{00}	7 584.222	7 625.698	7 669.202	7 691.715^{a} 7 691.722^{a}	7 714.882	7 762.900
2_{12}-1_{11}	14 860.644	14 940.245	15 023.716	15 066.908	15 111.342	
2_{02}-1_{01}	15 166.751	15 249.667	15 336.634	15 381.644^{a} 15 381.652^{a}	15 427.952	15 523.943
2_{11}-1_{10}	15 476.350	15 562.657	15 653.202	15 700.070	15 748.290	
2_{12}-3_{03}		19 551.770	19 397.039			
3_{13}-4_{04}		11 475.488	11 272.319			
			gauche Form			
1_{01}-0_{00}	7 732.534	7 773.494	78 16.439	7 838.652^{a} 7 838.664^{a}	7 861.513	7 908.874
2_{12}-1_{11}	15 145.721	15 224.416	15 306.909	15 349.587	15 393.477	
2_{02}-1_{01}	15 463.170	15 545.050	15 630.902	15 675.318^{a} 15 675.327^{a}	15 721.008	15 815.683
2_{11}-1_{10}	15 784.536	15 869.680	15 958.969	16 005.139	16 052.700	
2_{12}-3_{03}		17 414.644	17 282.819			
3_{13}-4_{04}		9 175.371	8 995.881			

[a] Splitting due to spin−rotation interaction.

TABLE 3: Rotational and Centrifugal Distortion Constants for Various Isotopomers of the syn Conformer

	^{82}Se	^{80}Se	^{78}Se	^{77}Se	^{76}Se
A, MHz	46 696.9 (95)	46 700.5420 (52)	46 703.1805 (49)	46719.8 (296)	46 726.4 (279)
B, MHz	3946.055 44 (38)	3968.4699 (46)	3991.991 33 (88)	4004.16796 (39)	4016.679 97 (39)
C, MHz	3638.170 78 (38)	3657.2330 (46)	3677.215 51 (88)	3687.554 16 (39)	3698.205 97 (39)
Δ_J, kHz	a	1.4030 (43)	1.41944 (148)	a	a
Δ_{JK}, kHz	a	−22.447 (43)	−22.580 (40)	a	a
Δ_K, kHz	a	754^{b}	754^{b}	a	a
δ_J, kHz	a	0.15823 (130)	0.16148 (132)	a	a
δ_K, kHz	a	6.65 (224)	6.91 (61)	a	a
Φ_{KJ}, Hz		−2.20 (18)	−2.24 (25)		

[a] Fixed at the ^{78}Se value. [b] Fixed to an ab initio value.

barrier of 5.9 cm^{-1} at the anti configuration itself. As for ethenethiol,[10] the ground vibrational state lies above this barrier.

Analysis of the Spectra. Selenium presents six isotopic forms, with the following natural abundances: ^{74}Se (0.87%), ^{76}Se (9%), ^{77}Se (7.6%), ^{78}Se (23.5%), ^{80}Se (49.8%) and ^{82}Se (9.2%). This large number of isotopic forms can be considered as a help for the identification of the lines but induces relatively crowded spectra in the millimeter wave region. Moreover, ^{77}Se has a nuclear spin $I = 1/2$, which causes some additional splitting for the lower J transitions, due to spin−rotation interaction. The calculated dipole moment indicates a stronger μ_a-type spectrum, for instance $\mu_a = 0.88$ D and $\mu_b = 0.25$ D were calculated for the syn conformer at the MP2/SDB-cc-pVTZ level.

The $J = 1-0$ lines were searched first between 7.5 and 8 GHz. The first broadband scans did not give reproducible results, excepted for the $J = 1-0$ transition of vinyl bromide,[25] which is present in the sample as an impurity and could not be completely eliminated. In some of our samples, vinyl bromide could be considered as the major product. In fact we noticed that the quality of the final sample depends on the purity of the precursor sample (divinyl diselenide) and on the nature of the solvents used at different stages of the synthesis. In some cases the main product present in the final sample was ethaneselenol, which could be identified following the data from ref 26.

After the successful observation and identification of the $J = 1-0$ transition of the syn conformer, the $J = 2-1$ transitions were observed. During the scans another set of lines was observed which was attributed to another conformer of etheneselenol, the gauche conformer. The $J = 1-0$ and $2-1$ transitions of this new conformer were identified for almost all the selenium isotopes.

Millimeter wave spectra were then recorded in order to assign more transitions, which are necessary for the determination of all the rotational constants. Due to the large density of lines (number of isotopic forms, low lying excited states, impurities, ...), only the lines belonging to the two most abundant isotopomers were searched, for both conformers. For the prediction of the spectra in the millimeter wave range, we used the calculated centrifugal distortion constants. The use of these ab initio calculated constants was really helpful in the assignment of the spectra. After the identification and the analysis of the millimeter wave spectra, some b-type transitions could then be successfully observed in the microwave region. The complete sets of experimental frequencies were fitted to a standard Watson's Hamiltonian, using the A reduction and I^r representation. The microwave frequencies are reported in Table 2, while the complete set of millimeter wave frequencies is available as supporting information. The rotational constants, together with the centrifugal distortion constants, are reported in Tables 3 and 4 for the syn and gauche conformers, respectively. For the less abundant species the A rotational constant was kept fixed. For the ^{77}Se species no spin rotation analysis was carried out and the mean frequencies were used in the analysis. Some ^{13}C lines were also observed in the microwave region, but their too small number prevented us from a more complete analysis.

In a second step, the monodeuterated species (−Se−D) were synthesized and their spectra recorded in the microwave region. In fact the deuterated sample contained about 50% of normal (nondeuterated) molecules. As shown in Figure 2, the microwave spectrum is rather dense. All the isotopic forms of selenium were observed for both conformers of the deuterated species. Due to the small amount of substance no millimeter-wave spectra were recorded. The corresponding measured

TABLE 4: Rotational and Centrifugal Distortion Constants for Various Isotopomers of the Gauche Conformer

	^{82}Se	^{80}Se	^{78}Se	^{77}Se	^{76}Se
A, MHz	45 101 (27)	45 096.7801 (52)	45 120.1607 (52)	45 409 (60)	45 148 (24)
B, MHz	4026.005 21 (39)	4048.0977 (22)	4071.2709 (32)	4083.2494 (12)	4095.565 76 (39)
C, MHz	3706.534 98 (39)	3725.4022 (21)	3745.1749 (32)	3755.4107 (12)	3765.954 26 (39)
Δ_J, kHz	a	1.72761 (240)	1.7459 (34)	a	a
Δ_{JK}, kHz	a	−25.897 (117)	−25.902 (123)	a	a
Δ_K, kHz	a	746^b	746^b	a	a
δ_J, kHz	a	0.19188 (118)	0.19500 (182)	a	a
δ_K, kHz	a	14.15 (103)	14.77 (161)	a	a
Φ_{KJ}, Hz		−6.33 (167)	−3.48 (220)		

[a] Fixed at the ^{80}Se value. [b] Fixed to an ab initio value.

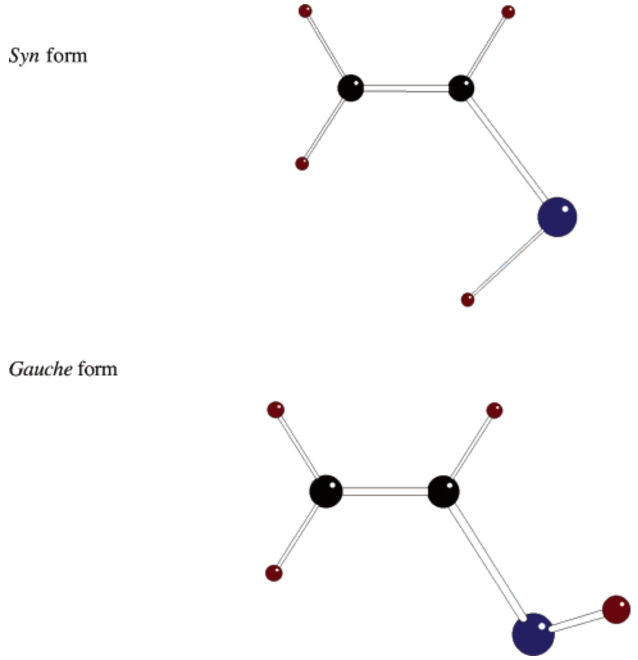

Figure 1. Observed conformers of etheneselenol.

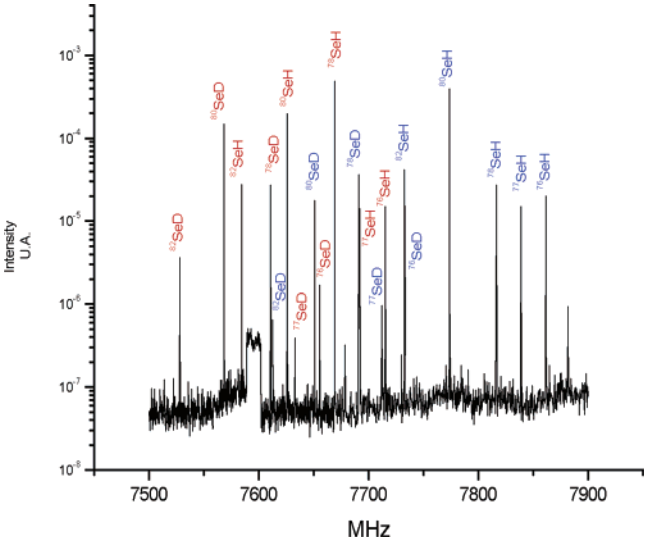

Figure 2. Spectral scan of the frequency range 7500−7900 MHz. The observed transition for each isotopic species is the $J = 1_{01}–0_{00}$ transition. Experimental conditions: mixture of CH_2CHSeH/CH_2CHSeD with 1 bar of neon; microwave power, 200 μW; 10 transient molecular signals added for each frequency step. The red labels are relative to the syn form, the blue ones to the gauche form; the intensity scale is arbitrary.

TABLE 5: Observed Microwave Frequencies for the Various Isotopomers of the Two Conformers of Etheneselenol-*d* (in MHz)

J'-J''	F'-F''	^{82}Se	^{80}Se	^{78}Se	^{76}Se
			syn Form		
1_{01}-0_{00}	1 1	7 527.885	7 568.343	7 610.755	7 655.264
	2 1	7 527.899	7 568.355	7 610.767	7 655.276
	0 1	7 527.917	7 568.375	7 610.786	7 655.296
2_{12}-1_{11}	1 1		14 771.283	14 852.011	
	2 1		14 771.313	14 852.039	
	3 2	14 694.303	14 771.329	14 852.057	14 936.748
	1 0	14 694.339	14 771.365	14 852.093	14 936.786
2_{02}-1_{01}	1 0		15 133.823	15 218.579	15 307.528
	3 2	15 052.988	15 133.840	15 218.598	15 307.543
	1 1	15 053.007	15 133.858		15 307.561
2_{11}-1_{10}	2 2		15 502.104	15 591.023	15 684.363
	2 1	15 417.315	15 502.117	15 591.034	15 684.376
	3 2	15 417.336	15 502.136	15 591.056	15 684.396
	1 1	15 417.376	15 502.174	15 591.096	15 684.435
			gauche Form		
1_{01}-0_{00}	1 1	7 612.589	7 650.907	7 691.045	7 733.133
	2 1	7 612.597	7 650.916	7 691.054	7 733.142
	0 1	7 612.606	7 650.925	7 691.066	7 733.150
2_{12}-1_{11}	1 1		14 949.013	15 025.892	15 106.490
	2 1	14 875.631	14 949.039	15 025.918	15 106.515
	3 2	14 875.641	14 949.047	15 025.926	15 106.524
	1 0		14 949.070		15 106.537
2_{02}-1_{01}	1 0	15 222.558	15 299.148	15 379.376	15 463.497
	3 2	15 222.567	15 299.157	15 379.385	15 463.506
	1 1	15 222.582		15 379.400	15 463.521
2_{11}-1_{10}	2 1	15 574.766	15 654.637	15 738.311	15 826.062
	3 2	15 574.782	15 654.653	15 738.329	15 826.078
	1 1	15 574.813	15 654.683	15 738.359	15 826.108

frequencies are reported in Table 5, and the respective molecular parameters in Tables 6 and 7.

Hyperfine Structure. Deuterium has a nuclear spin $I = 1$, and the corresponding lines are split into hyperfine components (see Figure 3). The magnitude of these splittings is between 10 and 40 kHz for the syn form and 8 and 30 kHz for the gauche form, which does not allow a complete resolution of the spectra in some cases. In the case of ^{77}Se the coupling between the two spins gives only a partially resolved spectrum, which has not been investigated. From the analysis of these hyperfine splittings, the diagonal quadrupole coupling constants of deuterium were determined and are reported in Tables 6 and 7. The values are consistent between isotopic species of the same conformer within the errors bars.

Molecular Structure. The two conformers observed for etheneselenol present comparable stabilities. For the same transition and for both conformers, the microwave signal was carefully recorded in order to compare the relative intensities, and no significant difference was found (we took into account the relative values of the dipole moment components, computed for both conformers).

The syn conformer presents a very small positive inertial defect: 0.0152 u Å^2 for ^{80}Se, indicating that it is a planar conformer. For comparison the inertial defect was found 0.046 u Å^2 for ethenol and 0.0312 u Å^2 for ethenethiol, for the same conformation. For the gauche conformer, the inertial defect found respectively for ethenol, ethenethiol, and etheneselenol

TABLE 6: Rotational and Deuterium Quadrupole Coupling Constants for Various Isotopomers of the Deuterated syn Conformer

	^{82}Se	^{80}Se	^{78}Se	^{76}Se
A, MHz	39 558 (38)	39 518 (26)	3 9 510 (30)	39 489 (27)
B, MHz	3944.7264 (14)	3966.8995 (13)	3990.1530 (13)	4014.5694 (13)
C, MHz	3583.1208 (15)	3601.4652 (13)	3620.6226 (13)	3640.7163 (16)
Δ_J,[a] kHz	2.81 (15)	2.85 (15)	2.79 (16)	2.89 (16)
χ_{aa}, kHz	−43.0 (43)	−46.2 (34)	−49.2 (41)	−44.3 (37)
$\chi_{bb} - \chi_{cc}$, kHz	186 (14)	169 (8)	171 (8)	171 (10)

[a] The other centrifugal distortion constants are fixed at the main species values.

TABLE 7: Rotational and Deuterium Quadrupole Coupling Constants for Various Isotopomers of the Deuterated Gauche Conformer

	^{82}Se	^{80}Se	^{78}Se	^{76}Se
A, MHz	39 909 (32)	39 895 (32)	39 926 (29)	39 960 (28)
B, MHz	3981.1196 (14)	4001.8956 (13)	4023.6633 (14)	4046.4949 (14)
C, MHz	3631.4889 (14)	3649.0318 (14)	3667.4023 (14)	3686.6577 (14)
Δ_J,[a] kHz	3.52 (16)	3.49 (16)	3.45 (16)	3.46 (16)
χ_{aa}, kHz	−29.1 (37)	−26.2 (41)	−31.9 (36)	−29.3 (36)
$\chi_{bb} - \chi_{cc}$, kHz	149 (15)	134 (9)	142 (11)	138 (11)

[a] The other centrifugal distortion constants are fixed at the main species values.

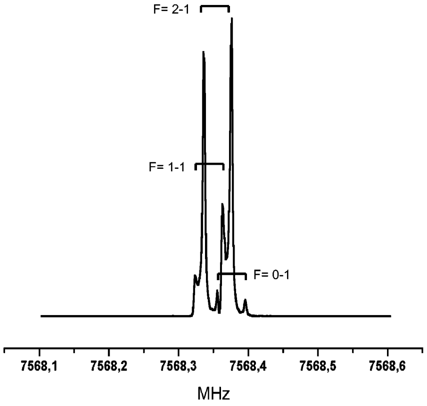

Figure 3. Hyperfine structure of the $J = 1_{01}$–0_{00} transition of CH_2-$CH^{80}SeD$: the $F = 1$-1 hyperfine component at 7568.343 MHz, the $F = 2$-1 hyperfine component at 7568.355 MHz, and the $F = 0$-1 hyperfine component at 7568.375 MHz.

is 0.0099, −0.198, and −0.394 u Å^2. This negative value seems to indicate a nonplanar conformer. Unfortunately the data corresponding to the deuterated isotopomers are not able to give a precise value of the rotational constant A (only low J a-type transitions were measured). The inertial defect for the deuterated species is then meaningless.

Nevertheless this confirms experimentally that the syn conformer, calculated to be the more stable one for the three vinylic compounds considered above, is planar in all cases. For the other conformer, the inertial defect increases in value from vinyl alcohol to etheneselenol, indicating a progressive departure from the planarity. This is congruent with the ab initio calculations.

We have not tried to calculate a substitution value for the Se−H internuclear distance because the H−D substitution does not fulfill the general conditions to correctly use the Kraitchman equations. Moreover, in the case of the syn form, the selenium atom lies on the principal a axis of inertia. For the ^{13}C species only the $J = 1$-0, 2-1, $K = 0$ transitions were securely identified, leading to the determination of (B + C) only. It is then difficult to obtain valuable structural information for the C−Se internuclear distance from the corresponding data.

For the syn conformer which is planar, assuming a cylindrical symmetry of the quadrupole coupling tensor around the Se−D bond leads to an angle $\Theta_{za} = 72°$ between the a-axis and the Se−H bond. This experimental value is in good agreement with the value obtained from the ab initio calculations: $\Theta_{za} = 80°$.

Conclusion

This paper reports the first spectroscopic study of etheneselenol. Two conformations, syn and gauche, were observed for this molecule, confirming the previous results obtained on ethenol and ethenethiol. The syn form was calculated to be the most stable and its planarity was confirmed experimentally. The rotational spectra of nine selenium isotopomers of etheneselenol and etheneselenol-d were observed in natural abundance for each conformer. Their analysis produced a large set of rotational constants but most of the structural information on both conformers was obtained by high-level ab initio calculations. The agreement between calculated and observed rotational constants is fairly good and we estimate that the calculated equilibrium structure is more reliable that any effective or substitution structure derived from our experimental data set. Our conformational analysis, which combines high-level quantum chemical calculations and high-resolution spectroscopic techniques such as microwave Fourier transform spectroscopy, will be extended to other unstable organic compounds containing a selenium atom, such as 3-buteneselenol for instance.[27]

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Supporting Information Available: Observed millimeter-wave frequencies for ^{78}Se and ^{80}Se isotopomers of the two conformers of etheneselenol. This material is available free of charge via the Internet at http://pubs.acs.org.

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