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Spectroscopic and Quantum Chemical Study of the Novel Compound Cyclopropylmethylselenol

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An investigation into the properties of the novel compound cyclopropylmethylselenol has been undertaken by use of Stark-modulation microwave spectroscopy and high-level quantum chemical calculations. Ground-state spectra belonging to six isotopomers of a single conformer of the molecule were recorded and assigned. This conformer, predicted to be the lowest in energy by a series of quantum chemical calculations, possesses a synclinal arrangement of the H−C−C−Se atoms. In addition to the assignment of these ground-state spectra, transitions attributable to vibrationally excited states of the ^{78}Se- and ^{80}Se-containing isotopomers were identified. A tentative assignment of these excited-state spectra to specific vibrational modes has been made with the assistance of a density functional theory calculation at the B3LYP/6-311++G(3df,2pd) level of theory. Close agreement was found between experimental ground-state rotational constants and ab initio equilibrium values calculated at the MP2/aug-cc-pVTZ level of theory. Good agreement was also noted between certain r_s principal axis coordinates of atoms in the molecule and the corresponding ab initio r_e values. Limited evidence in favor of the formation of a weak intramolecular hydrogen bond between the H atom of the selenol group and electron density associated with the cyclopropyl ring is discussed.

Introduction

The ability of selenols to form intramolecular hydrogen bonds in the gas phase was first demonstrated in the case of 3-buteneselenol.[1] The lowest-energy conformer of this molecule is stabilized by an internal hydrogen bond between the H atom of the selenol group and the π electrons of the double bond. Few selenols have to date been studied by microwave (MW) spectroscopy, and no other example of a selenol forming an intramolecular hydrogen bond has been found. The fact that so few selenols have been studied is likely to be in part a consequence of their toxicity, instability toward air, and powerfully obnoxious odors.

The subject of the current investigation, namely, cyclopropylmethylselenol, has been chosen in order to allow a direct comparison with the analogous alcohol (C_3H_5CHOH)[2−4] and thiol (C_3H_5CHSH)[5] molecules to be made. Both of these molecules have been shown to possess intramolecular hydrogen bonds, formed between the −XH (X = O, S) group and electron density along the edge of the cyclopropyl ring. It is therefore of interest to determine whether cyclopropylmethylselenol can be stabilized by a similar interaction.

Figure 1 shows the five possible conformers of cyclopropylmethylselenol. It can be seen that conformers II, III, and V are capable of forming an intramolecular H bond by means of a close approach between a Se−H group and the center of a C−C bond in the cyclopropyl group. Such an interaction is not possible for conformers I and IV.

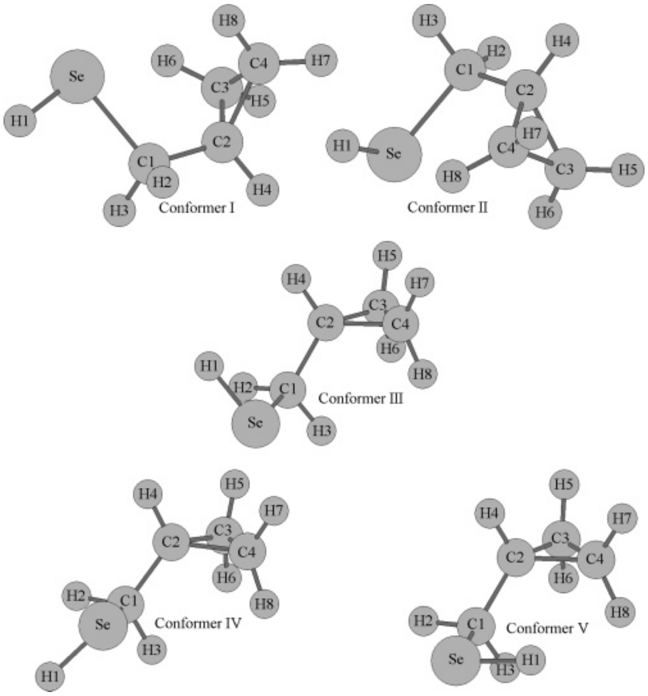

Figure 1. Structures of the five conformers of cyclopropylmethylselenol, as obtained from geometry optimizations performed at the MP2/aug-cc-pVTZ level of theory with the Gaussian 03 electronic structure package.

Experimental Section

Microwave Experiment. The microwave spectrum of cyclopropylmethylselenol was recorded in the 22−62 GHz

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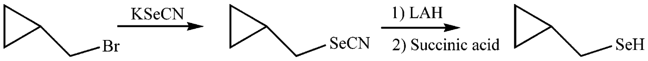
SCHEME 1



frequency range by means of Stark-modulation microwave spectroscopy on the microwave spectrometer at the University of Oslo. Details of the design and operation of this device, which possesses a 2 m Stark cell, have been given elsewhere.[6] In addition to the standard Stark-modulation experiment, a number of rotational transitions were observed by using a radio frequency microwave double-resonance method, of the type originally employed by Wodarczyk and Wilson.[7] The Stark cell was cooled with a quantity of solid CO_2 to approximately -50 °C during the course of the experiment, with the aim of increasing spectral intensity.

Preparation of Cyclopropylmethylselenol. Cyclopropylmethylselenol has been prepared starting from selenocyanic acid, cyclopropylmethyl ester, by an approach similar to that previously reported for 3-buteneselenol (Scheme 1).[1]

Selenocyanic Acid, Cyclopropylmethyl Ester. In a 100 mL two-necked flask equipped with a stirring bar and a nitrogen inlet were introduced the bromomethylcyclopropane (2.70 g, 20 mmol), dry acetonitrile (50 mL), and potassium selenocyanate (3.02 g, 21 mmol). After the mixture was stirred for 3 h at 70 °C, the precipitated potassium bromide was filtered and the solvent was removed in vacuo. The selenocyanate was purified by distillation in vacuo and obtained in 87% yield (2.80 g, 17.4 mmol); bp 47 °C (0.1 mmHg). ^{1}H NMR (400, MHz, $CDCl_3$) δ 0.42 (m, 2H, 1H of each CH_2 of the cycle); 0.79 (m, 2H, 1H of each CH_2 of the cycle); 1.29 (m, 1H, $^{3}J_{HH} = 7.6$ Hz, CH-CH_2-Se); 3.07 (d, 2H, $^{3}J_{HH} = 7.6$ Hz, $^{2}J_{SeH} = 15.2$ Hz, CH_2Se). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.44 (t, $^{1}J_{CH} = 160.6$ Hz, CH_2 cycle); 12.4 (d, $^{1}J_{CH} = 161.4$ Hz, CH); 35.9 (t, $^{1}J_{CH} = 139.7$ Hz, $^{1}J_{SeC} = 49.0$ Hz (d), CH_2Se); 101.9 (s, CN). ^{77}Se NMR (57.2 MHz, $CDCl_3$) δ 215.0. HRMS Calcd for C_5H_7NSe: 160.9743. Found: 160.974.

Cyclopropylmethylselenol. The apparatus previously described for the reduction of dibromopropargylphosphine was used.[8] A 50-mL two-necked flask containing succinic acid (1.18 g, 10 mmol) diluted in tetraglyme (10 mL) was attached to 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 selenocyanic acid, cyclopropylmethyl 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, cyclopropylmethylselenol was distilled off in vacuo (10^{-1} mbar) from the reaction mixture. A first cold trap (-35 °C) selectively removed the less volatile products, and cyclopropylmethylselenol 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 attached to the microwave spectrometer. Yield 90%; bp ≈ -40 °C (0.1 mmHg). The sample contains 1−3% 3-buteneselenol, an isomerization product. No decomposition was observed after several months in a freezer (-30 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.56 (td, 1H, $^{3}J_{HH} = 6.8$ Hz, $^{4}J_{HH} = 1.8$ Hz, $^{1}J_{SeH} = 46.8$ Hz (d), SeH); 0.09 (m, 2H, 1H of each CH_2 of the cycle); 0.53 (m, 2H, 1H of each CH_2 of the cycle); 1.00 (m, 1H, $^{3}J_{HH} = {}^{3}J_{HH} = 6.8$ Hz, $^{4}J_{HH} = 1.8$ Hz, CH−CSe); 2.42 (dd, 2H, $^{3}J_{HH} = 6.8$ Hz, CH_2Se). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.39 (t, $^{1}J_{CH} = 162.2$ Hz, CH_2 cycle); 15.3 (d, $^{1}J_{CH} = 165.4$ Hz, CH); 23.8 (t, $^{1}J_{CH} = 143.0$ Hz, $^{1}J_{SeC} = 46.6$ Hz (d), CH_2Se). ^{77}Se NMR (57.2 MHz, $CDCl_3$) δ -3.5. HRMS Calcd for $C_4H_8{}^{80}Se$: 135.9791. Found: 135.978.

Deuterated cyclopropylmethylselenol ($C_3H_5CH_2SeD$) was generated in situ by admitting a small volume of D_2O vapor from above a liquid sample at room temperature into the cavity of the spectrometer, which already contained an amount of cyclopropylmethylselenol vapor giving a pressure of a few pascals. Exchange of a single D atom with the H atom of the selenol group occurred readily, resulting in an estimated 50% deuteration.

Results

Quantum-Chemical Calculations. A number of quantum-chemical calculations were performed for cyclopropylmethylselenol, with the aim of aiding the assignment of the microwave spectrum and providing useful structural information. Calculations were performed by use of the Gaussian 03 electronic structure package[9] in conjunction with the University of Oslo's 64-processor HP Superdome computer.[10] The geometries of the five possible conformations of the molecule were optimized in a series of self-consistent field calculations, in which the aug-cc-pVTZ basis set[11] was utilized. The effects of electron correlation were taken into account in these calculations by the use of second-order Møller−Plesset perturbation theory (MP2).[12] A recent study of the closely related molecule cyclopropylmethylphosphine[13] showed that the use of Dunning's extensive, correlation-consistent, aug-cc-pVTZ basis set, which incorporates polarized functions for valence electrons and is augmented by additional diffuse functions, can provide accurate estimates of rotational constants when used in MP2 calculations. Specifically, the values of the equilibrium rotational constants from calculations at this level of theory were found to be within ∼1% of the corresponding values of experimentally determined, ground-state rotational constants.

A second set of calculations were undertaken, in which a density functional theory method was used to predict the values of the quartic centrifugal distortion constants in Watson's A-reduction,[14] to estimate the frequencies of the normal modes of vibration, and to evaluate the optimized geometry of each of the five possible conformers. To this end, the B3LYP hybrid functional (Becke's three-parameter hybrid functional,[15] employing the Lee, Yang, and Parr correlational functional[16]) was employed, together with the 6-311++G(3df,2pd) basis set. Since the calculation of centrifugal distortion constants can be a computationally demanding task, the use of a density functional theory method was preferred to a MP2 calculation, as the former will, in general, require less computational effort. It is the experience of the authors that the calculation of the quartic centrifugal distortion constants at the B3LYP/6-311++G(3df,2pd) level of theory provides values within approximately 10% of the experimental values.[13]

The values of the spectroscopic constants obtained at the MP2/aug-cc-pVTZ and B3LYP/6-311++G(3df,2pd) levels of theory are presented in Table 1, while Figure 1 shows the structures of the five possible conformers of cyclopropylmethylselenol, as predicted by the MP2/aug-cc-pVTZ calculations, drawn to scale.

Assignment of Conformer V. The calculated relative energies of the five conformers of cyclopropylmethylselenol at the MP2/aug-cc-pVTZ and B3LYP/6-311++G(3df,2pd) levels of theory are presented in Table 2. It can be seen that conformer

TABLE 1: Comparison of Experimental and Calculated Spectroscopic Constants[a] for Conformer V of Cyclopropylmethylselenol

spectoscopic constant	B3LYP/ 6-311++(3df,2pd)	MP2/aug-cc-pVTZ	experiment
A/MHz	11 247.9427	11 123.7894	11 076.8(50)
B/MHz	1282.5706	1344.7932	1319.7659(46)
C/MHz	1213.3944	1267.6068	1244.8829(46)
Δ_J/kHz	0.262 306		0.2699(23)
Δ_{JK}/kHz	−2.642 531		−2.5652(52)
Δ_K/kHz	29.161 521		29.161 521[b]
δ_J/kHz	0.0270 18		0.027 018[b]
δ_K/kHz	1.201 876		1.201 876[b]

[a] Constants given are for the $C_3H_5CH_2{}^{80}SeH$ isotopomer. Uncertainties represent one standard deviation. [b] Fixed at the value obtained from B3LYP/6-311++G(3df,2pd) density functional calculations.

TABLE 2: Comparison of the Relative Energies of Five Conformers of Cyclopropylmethylselenol, Obtained from ab Initio Calculations and Experiment

	energy of conformer (kJ mol^{-1})				
method	I	II	III	IV	V
B3LYP/6-311++G(3df,2pd)	+13.5	+7.5	+1.6	+2.2	0.0
MP2/aug-cc-pVTZ	+9.3	+2.3	+1.9	+2.6	0.0

V is consistently predicted to be the lowest in energy; therefore, initial attempts to assign the microwave spectrum of cyclopropylmethylselenol focused on this conformer. The geometry optimization performed for this conformer by use of density functional theory at the B3LYP/ 6-311++G(3df,2pd) level of theory predicted that the components of the molecular electric dipole moment along the principal inertial axes take the values $\mu_a = 1.67$ D, $\mu_b = -0.18$ D, and $\mu_c = 0.24$ D. It is therefore expected that conformer V should display an observable *a*-type rotational spectrum only. A prediction of the spectrum of this conformer was obtained by the use of rotational constants from a geometry optimization at the MP2/aug-cc-pVTZ level of theory and quartic centrifugal distortion constants calculated at the B3LYP/6-311++G(3df,2pd) level. This model enabled the assignment of a number of transitions belonging to the parent isotopomer of cyclopropylmethylselenol, conformer V. The use of radio frequency microwave double-resonance experiments to identify unambiguously a number of transitions having K_a equal to 3 or 4 was of assistance in this process. The frequencies of individual rotational transitions were analyzed in a least-squares fit, by use of Sørensen's Rotfit program.[17] The spectroscopic constants obtained in this way are presented in Table 3, while the measured transition frequencies and residual differences between the observed and predicted frequencies are given in the Supporting Information, Table 1S.

Having assigned the spectrum of the most abundant isotopomer, it was then possible to identify transitions belonging to less abundant isotopomers. In total, spectra due to five selenium-substituted isotopomers of conformer V were assigned, namely, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, and ^{82}Se, which have abundances of 9.4%, 7.6%, 23.8%, 49.6%, and 8.7%, respectively. The spectroscopic constants obtained for these additional isotopomers are included in Table 3, and the observed transition frequencies and residuals are in the Supporting Information, Tables 2S−5S. The spectra of each of these species were typical of a nearly-prolate asymmetric rotor, in which only the *a*-type rotational transitions were sufficiently intense to allow their observation. As previously mentioned, a B3LYP/6-311++G(3df,2pd) calculation predicted that μ_a will be the largest component of the molecular electric dipole moment by a significant margin, which is consistent with the observed spectra.

After the ground-state rotational spectra of five isotopomers of cyclopropylmethylselenol were assigned, a number of transitions belonging to vibrationally excited states were recorded by the radio frequency microwave double-resonance method. It was possible to assign spectra belonging to four vibrationally excited states of conformer V; two of these correspond to the isotopomer $C_3H_5CH_2{}^{78}SeH$ and two correspond to $C_3H_5CH_2{}^{80}SeH$. The spectroscopic constants obtained from the least-squares analysis of these states, labeled 78V*a*, 78V*b*, 80V*a*, and 80V*b*, are given in Table 4, while the transition frequencies and residuals are given in Tables 7S−10S in the Supporting Information. These states are believed to correspond to the first and second excited states of a single mode of vibration. A calculation of the vibrational frequencies of the molecule at the B3LYP/6-311++(3df,2pd) level of theory predicted that the lowest energy vibrational mode would be the torsional motion about the C1−C2 bond (94.3 cm^{-1}). Although a definitive assignment of these excited-state spectra is not possible from the available data, it is considered probable that they correspond to the torsional motion predicted by the DFT calculation. A similar DFT calculation performed at the same level of theory for the closely related molecule cyclopropylmethylphosphine[13] gave a similar result, with the torsional motion about the C1−C2 bond predicted to be the lowest in energy (~90 cm^{-1}).

The ground-state rotational spectrum of the isotopomer $C_3H_5CH_2{}^{80}SeD$ was measured for a deuterium-enriched sample of cyclopropylmethylselenol prepared according to the procedure outlined above. A total of 77 *a*-type, R-branch transitions were identified as belonging to this isotopomer. The least-squares fit of these transitions gave the spectroscopic constants included in Table 3. The observed rotational transition frequencies for this isotopomer are presented in the Supporting Information in

TABLE 3: Experimentally Determined Spectroscopic Constants for Five Isotopomers of Conformer V of Cyclopropylmethylselenol

spectroscopic constant	isotopomer					
	$C_3H_5CH_2{}^{76}SeH$	$C_3H_5CH_2{}^{77}SeH$	$C_3H_5CH_2{}^{78}SeH$	$C_3H_5CH_2{}^{80}SeH$	$C_3H_5CH_2{}^{82}SeH$	$C_3H_5CH_2{}^{80}SeD$
A/MHz	11 127.7107[a]	11 126.6114[a]	11 052.7(32)	11 076.8(50)	11 121.9674[a]	10 653.6122[a]
B/MHz	1344.833(45)	1337.262(58)	1331.1016(46)	1319.7659(46)	1309.343(53)	1317.466(31)
C/MHz	1263.756(51)	1259.884(63)	1255.0126(43)	1244.8829(46)	1234.772(54)	1237.802(34)
Δ_J/kHz	0.289(8)	0.261(6)	0.2765(18)	0.2699(23)	0.276(5)	0.295(4)
Δ_{JK}/kHz	−2.602(13)	−2.353(15)	−2.5792(32)	−2.5652(52)	−2.368(13)	−2.672(8)
Δ_K/kHz	29.161 521[b]	29.161 521[b]	29.161 521[b]	29.161 521[b]	29.161 521[b]	29.161 521[b]
δ_J/kHz	0.027 018[b]	0.027 018[b]	0.027 018[b]	0.027 018[b]	0.027 018[b]	0.027 018[b]
δ_K/kHz	1.201 876[b]	1.201 876[b]	1.201 876[b]	1.201 876[b]	1.201 876[b]	1.201 876[b]
σ^c/kHz	0.10	0.15	0.14	0.17	0.13	0.23
N[d]	26	36	134	116	44	77

[a] Fixed at the value obtained from a geometry optimization at the MP2/aug-cc-pVTZ level of theory. Uncertainties represent one standard deviation. [b] Fixed at the value obtained from B3LYP/6-311++G(3df,2pd) density functional calculation. [c] Root-mean-square deviation of fit. [d] Number of transitions.

TABLE 4: Experimentally Determined Spectroscopic Constants for Four Vibrationally Excited States of Conformer V of Cyclopropylmethylselenol

spectroscopic constant	state			
	78V*a*	78V*b*	80V*a*	80V*b*
A/MHz	11 052.7[a]	11 052.7[a]	11 076.8[a]	11 076.8[a]
B/MHz	1328.799(77)	1336.49(71)	1317.541(62)	1325.69(93)
C/MHz	1253.269(77)	1240.88(72)	1243.059(67)	1230.83(94)
Δ_J/kHz	0.282(9)	0.368(5)	0.254(5)	0.280(7)
Δ_{JK}/kHz	−2.54(2)	−2.817(15)	−2.557(14)	−2.639(18)
Δ_K/kHz	29.161 521[b]	29.161 521[b]	29.161 521[b]	29.161 521[b]
δ_J/kHz	0.027 018[b]	0.027 018[b]	0.027 018[b]	0.027 018[b]
δ_K/kHz	1.201 876[b]	1.201 876[b]	1.201 876[b]	1.201 876[b]
σ[c]/kHz	0.17	0.08	0.19	0.14
N[d]	32	40	54	56

[a] Fixed at the value obtained from a geometry optimization for the ground state of the corresponding isotopomer at the MP2/aug-cc-pVTZ level of theory. Uncertainties represent one standard deviation. [b] Fixed at the value obtained from a B3LYP/6-311++G(3df,2pd) density functional calculation performed for the ground state of the corresponding isotopomer. [c] Root-mean-square deviation of fit. [d] Number of transitions.

Table 6S, together with the residual errors from the final cycle of the least-squares fit.

Failure To Detect Conformers I−IV. Having assigned transitions in the ground and excited-state spectra of five isotopomers of conformer V from an isotopically normal sample of cyclopropylmethylselenol, an attempt was made to identify transitions belonging to other conformers of the molecule. Predictions of the spectra of conformers I−IV were made in the same manner as for conformer V, that is, by the use of rotational constants from ab initio geometry optimizations at the MP2/aug-cc-pVTZ level of theory and quartic centrifugal distortion constant obtained from DFT calculations at the B3LYP/6-311G++(3df,2pd) level. No transitions attributable to conformers I−IV could be identified by use of these predictions, despite the use of both conventional Stark-modulation spectroscopy and radio frequency microwave double-resonance (RFMWDR) experiments. It is considered likely that this is in part a consequence of the difference in energy between conformer V and the other conformers, and partly a result of the numerous selenium isotopes leading to spectral intensity being divided among different isotopomers. In these conditions, the detection of weak transitions in an already crowded spectrum becomes difficult.

r_s Coordinates of Atoms in Cyclopropylmethylselenol. The isotopic substitution of an atom in a molecule allows the coordinates of that atom to be determined in the principal inertial axis system of the parent molecule. This can be achieved by solving Kraitchmann's equations,[18] by use of the equilibrium moments of inertia of the relevant species. In the case of a nonplanar asymmetric rotor, the modulus of the principal axis coordinate α_s of the substituted atom can be obtained from

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

where $\Delta P_\alpha = (-\Delta I_\alpha + \Delta I_\beta + \Delta I_\gamma)$ and $\Delta I_\alpha = I'_\alpha - I_\alpha$. By cyclically permuting α, β, and γ over *a*, *b*, and *c*, the position of a nucleus relative to the three principal inertial axes may be determined. While experimental equilibrium moments of inertia were not obtained during the current investigation, Kraitchmann's equations may also be solved by use of ground-state moments of inertia, yielding the r_s (substitution) coordinates of the substituted atom.[19]

Since only *a*-type spectra were observed for the various isotopomers studied, the errors associated with the values of the *A* rotational constants obtained for these isotopomers are substantially larger than the errors in *B* and *C*. As a consequence of this, when the r_s coordinates of atoms are calculated, the *a* coordinate could be determined more accurately than either *b* or *c*. The values obtained for the modulus of the *a*-substitution coordinate of the Se atom were 125.621, 125.453, 127.871, and 129.006 pm, when calculated by use of the rotational constants from the ^{76}Se, ^{77}Se, ^{78}Se, and ^{82}Se isotopomers of conformer V, respectively, with the ^{80}Se isotopomer used as the parent. The approximate r_e value of this parameter, as obtained from an ab initio calculation at the MP2/aug-cc-pVTZ level of theory, was −125.654 pm, which constitutes a good agreement. A similar process was followed with the rotational constants for the deuterated cyclopropylmethylselenol, to determine the position of the H atom that is bonded to selenium. The modulus of the r_s *a* coordinate for this atom was found to take a value of 76.599 pm, which compares favorably with the ab initio value of −76.099 pm.

Intramolecular Hydrogen Bonding. A comparison between the experimental ground-state rotational constants obtained for conformer V and the r_e values generated by means of an ab initio calculation at the MP2/aug-cc-pVTZ level of theory is made in Table 1. It can be seen that there is close agreement (i.e., within 1−2%) between the corresponding pairs of constants, which suggests that the structure yielded by the calculation is an accurate prediction of the structure of this conformer, neglecting the minor differences between r_0 and r_e geometries. Similarly, the agreement between the r_s *a* coordinates of atoms in the −SeH group and the corresponding equilibrium principal axis coordinates also suggests that the ab initio structure is valid.

Full ab initio structures for the five conformers of cyclopropylmethylselenol were calculated at the MP2/aug-cc-pVTZ level of theory. The structure obtained in this way for conformer V is given in Table 5, while the structures of conformers I−IV are presented in the Supporting Information in Table 11S.

A careful analysis of the ab initio structure of conformer V provides little conclusive evidence in favor of the formation of an intramolecular hydrogen bond. The distance between the H atom of the selenol group and the midpoint of the C−C bond along the edge of the cyclopropyl group is 290.97 pm, which is not substantially different from the sum of the van der Waals radii of these groups (∼290 pm).[20] Similarly, the Se−H bond distance, which would be expected to lengthen upon H bond formation, is constant among the three synclinal conformers. It is necessary to qualify these observations by noting that any changes in these parameters upon formation of a hydrogen bond would be minor, and, therefore, the formation of a weak intramolecular hydrogen bond cannot be precluded. Indeed, an argument supporting the formation of such a bond can be constructed on the observation that the only conformer of the molecule which had a sufficiently high population to allow its spectra to be recorded was that in which the formation of a stabilizing hydrogen bond was most favorable.

It is also of interest to compare the structure of cyclopropylmethylselenol with those of the analogous alcohol[2−4] and thiol,[5] which are both stabilized by intramolecular hydrogen bonding. To this end, geometry optimizations were performed at the MP2/aug-cc-pVTZ level of theory for the lowest-energy conformers of cyclopropylmethylthiol and cyclopropylmethanol, which both correspond to cyclopropylmethylselenol, conformer V. The structures obtained from these calculations are included in Table 5. It can be seen that the structure of the cyclopropyl ring does

TABLE 5: Geometries of H-Bonded Conformers of Cyclopropylmethylselenol,[a] Cyclopropylmethylthiol, and Cyclopropylmethanol from ab Initio Geometry Optimizations at the MP2/Aug-cc-pVTZ Level of Theory

structural parameter	X = Se	X = S	X = O
Bond Lengths (pm)			
$r(H_1-X)$	145.3	133.8	96.4
$r(X-C_1)$	195.0	182.4	142.6
$r(C_1-H_2)$	109.0	109.1	108.9
$r(C_1-H_3)$	108.9	109.1	109.7
$r(C_1-C_2)$	149.6	149.8	149.8
$r(C_2-H_4)$	108.2	108.2	108.2
$r(C_2-C_3)$	150.6	150.5	150.3
$r(C_2-C_4)$	150.3	150.4	150.8
$r(C_3-H_5)$	107.9	107.9	107.9
$r(C_3-H_6)$	108.0	108.0	108.0
$r(C_3-C_4)$	151.0	150.9	150.7
$r(C_4-H_7)$	107.9	107.9	107.9
$r(C_4-H_8)$	108.1	108.0	108.1
Bond Angles (deg)			
$\angle(H_1,X,C_1)$	93.8	95.5	106.9
$\angle(X,C_1,C_2)$	112.6	112.9	112.5
$\angle(H_2,C_1,C_2)$	111.9	111.4	111.1
$\angle(H_3,C_1,C_2)$	110.9	110.4	109.0
$\angle(C_1,C_2,C_3)$	118.7	118.7	118.8
$\angle(C_1,C_2,C_4)$	118.4	118.3	117.9
$\angle(C_1,C_2,H_4)$	115.4	115.3	115.5
$\angle(C_2,C_3,H_5)$	118.0	118.0	117.9
$\angle(C_2,C_3,H_6)$	117.2	117.3	117.3
$\angle(C_2,C_4,H_7)$	118.4	118.4	118.3
$\angle(C_2,C_4,H_8)$	116.8	117.0	117.2
Dihedral Angles (deg)			
$\angle(H_1,X,C_1,C_2)$	−56.0	−54.9	−49.6
$\angle(X,C_1,C_2,C_3)$	154.5	154.8	152.0
$\angle(X,C_1,C_2,C_4)$	84.9	85.2	82.7
$\angle(X,C_1,C_2,H_4)$	−59.6	−59.2	−61.5
$\angle(H_1,X,C_1,H_2)$	−177.7	−176.3	−170.9
$\angle(H_1,X,C_1,H_3)$	67.1	68.4	72.7
$\angle(C_1,C_2,C_3,H_5)$	144.1	144.2	144.7
$\angle(C_1,C_2,C_3,H_6)$	−0.8	−0.7	0.1
$\angle(C_1,C_2,C_4,H_7)$	−143.6	−143.5	−143.5
$\angle(C_1,C_2,C_4,H_8)$	1.3	1.5	1.9

[a] Further conformers are listed in Supporting Information Table 11S.

not differ greatly among these three molecules, which is to be expected. Three parameters that do differ significantly are the bond lengths H1−X and X−C1, and the bond angle H1−X−C1 (X = O, S, Se), where the values belonging to the selenol and the thiol are fairly close, whereas the substitution of an oxygen atom causes larger changes. This is consistent with the relative electronegativities of these atoms, as oxygen has a significantly larger electronegativity (3.44) than either sulfur (2.58) or selenium (2.55).[20] This pattern is also reflected in the hydrogen-bond distance between H1 and the midpoint of the C2−C4 bond, which takes a value of 260.3, 282.9, and 291.0 pm for the alcohol, thiol, and selenol, respectively. As expected, this suggests that the alcohol has the strongest hydrogen bond of these species, with a smaller difference in bond strength between the thiol and selenol.

Conclusions

The microwave spectrum of cyclopropylmethylselenol was recorded on a Stark-modulation microwave spectrometer in the 12−62 GHz frequency interval. Transitions due to six isotopomers of a single synclinal conformer of the molecule were observed and assigned. In addition, transitions belonging to four vibrationally excited species were observed and a tentative assignment to specific vibrational modes was made, with the aid of density functional theory calculations.

It was noted that the agreement between the experimental ground-state rotational constants obtained for the preferred conformer were in close agreement with the corresponding r_e values from an ab initio calculation at the MP2/aug-cc-pVTZ level of theory. Assignment of the *a*-type spectra of a number of isotopically substituted species enabled the r_s *a* coordinates of the atoms in the −SeH group to be evaluated in the principal inertial axis system. The values calculated for these parameters were found to agree closely with the corresponding values obtained from the MP2/aug-cc-pVTZ calculation.

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

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