

## A Microwave and Quantum Chemical Study of Cyclopropaneselenol

Rajmund Mokso,<sup>†</sup> Harald Møllendal,<sup>\*,‡</sup> and Jean-Claude Guillemin<sup>‡</sup>

Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway, and Sciences Chimiques de Rennes, École Nationale Supérieure de Chimie de Rennes-CNRS, F-35700 Rennes, France

Received: May 10, 2008; Revised Manuscript Received: June 13, 2008

The microwave spectrum of cyclopropaneselenol,  $C_3H_5SeH$ , has been investigated in the 21.9–80 GHz frequency range. The microwave spectra of the ground vibrational state of five isotopologues of cyclopropaneselenol ( $C_3H_5^{82}SeH$ ,  $C_3H_5^{80}SeH$ ,  $C_3H_5^{78}SeH$ ,  $C_3H_5^{77}SeH$ , and  $C_3H_5^{76}SeH$ ) of one conformer, as well as the spectra of two vibrationally excited states of each of the  $C_3H_5^{80}SeH$  and  $C_3H_5^{78}SeH$  isotopologues of this rotamer, have been assigned. The H–C–Se–H chain of atoms is synclinal in this conformer, and there is no indication of further rotameric forms in the microwave spectrum. The *b*-type transitions of the ground vibrational state of the more abundant species  $C_3H_5^{80}SeH$  and  $C_3H_5^{78}SeH$  were split into two components, which is assumed to arise from tunneling of the proton of the selenol group between two equivalent synclinal potential wells. The tunneling frequencies were 0.693(55) MHz for  $C_3H_5^{80}SeH$  and 0.608(71) MHz for  $C_3H_5^{78}SeH$ . The microwave study has been augmented by high-level density functional and ab initio quantum chemical calculations, which indicate that the H–C–Se–H dihedral angle is  $\approx 75^\circ$  from synperiplanar ( $0^\circ$ ).

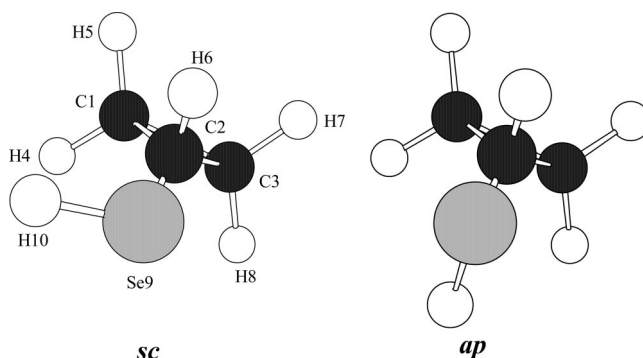
## Introduction

The structural, conformational and dynamical properties of cyclopropanols and cyclopropanethiol have been the themes for several microwave (MW) studies. These investigations have shown that cyclopropanol ( $C_3H_5OH$ ),<sup>1</sup> 1-cyclopropylcyclopropanol ( $C_3H_4(OH)C_3H_4$ ),<sup>2</sup> and 1-ethenylcyclopropan-1-ol ( $C_3H_4(OH)C=CH_2$ )<sup>3</sup> prefer a H–C–O–H synclinal (obsolete gauche) conformation in their lowest-energy forms. This is also the case for the related cyclopropyl methyl ether ( $C_3H_5OCH_3$ )<sup>4,5</sup> for its H–C–O–CH<sub>3</sub> link of atoms.

A very recent MW study<sup>6</sup> of the thiol congener, cyclopropanethiol ( $C_3H_5SH$ ), demonstrated that this compound prefers a conformation in which the H–C–S–H link of atoms is synclinal, actually  $76(5)^\circ$  from synperiplanar ( $0^\circ$ ). It should also be mentioned that the preferred form of cyclopropyl methyl thioether ( $C_3H_5SCH_3$ ) has a synclinal arrangement for the H–C–S–CH<sub>3</sub> chain.<sup>7</sup>

The recent syntheses of functionalized selenols<sup>8–10</sup> have made it possible to perform MW studies of many new members of this interesting class of compounds. The MW spectra of 3-buteneselenol ( $HSeCH_2CH_2C=CH_2$ ),<sup>11</sup> cyclopropylmethylselenol ( $C_3H_5CH_2SeH$ ),<sup>12</sup> and 3-butyne-1-selenol ( $HSeCH_2CH_2C\equiv CH$ )<sup>13</sup> have already been reported. The current study of cyclopropaneselenol ( $C_3H_5SeH$ ) was undertaken as an extension of the selenol studies. We were especially interested in comparing the conformational and dynamical properties of this compound with the oxygen ( $C_3H_5OH$ )<sup>1</sup> and sulfur ( $C_3H_5SH$ )<sup>6</sup> analogues.

Two rotameric forms can be envisaged for cyclopropaneselenol in which the H–C–Se–H link of atoms forms a synclinal or an antiperiplanar arrangement ( $180^\circ$  from synperiplanar). These two rotamers are henceforth called *sc* and *ap*, respectively,



**Figure 1.** Models of the two stable conformers, *sc* and *ap*, of cyclopropaneselenol according to the quantum chemical predictions. Atom numbering is given on *sc*. The H6–C2–Se9–H10 dihedral angle is synclinal in *sc* and antiperiplanar in *ap*. The MW spectrum of *sc* has been assigned in this work.

and they are sketched in Figure 1, where the atom numbering is also given.

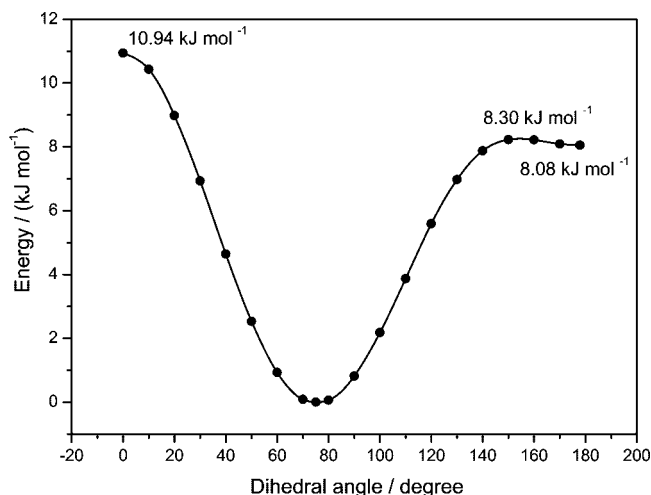
Interestingly, *sc* would be expected to exhibit the ability to undergo rovibrational transitions between states of opposite parity in the torsional vibration of the thiol top resulting in “tunneling” between the two equivalent synclinal potential wells. This phenomenon has already been observed in cyclopropanol<sup>1</sup> and cyclopropanethiol.<sup>6</sup> It also occurs for selenols and has been reported in at least one case, namely, for the C–C–Se–H synclinal form of ethaneselenol ( $CH_3CH_2SeH$ ).<sup>14</sup> The rovibrational transitions allowed the determination of accurate torsional energy differences in these cases.

This first study of the MW spectrum of  $C_3H_5SeH$  was undertaken to determine the conformational and tunneling properties of this compound. The MW study has been augmented by quantum chemical calculations performed at high levels of theory. The current calculations were conducted to obtain information for use in assigning the MW spectrum and investigating the properties of the potential-energy hypersurface.

\* To whom correspondence should be addressed. Tel: +47 2285 5674. Fax: +47 2285 5441. E-mail: harald.mollendal@kjemi.uio.no.

<sup>†</sup> University of Oslo.

<sup>‡</sup> Ecole Nationale Supérieure de Chimie de Rennes.



**Figure 2.** B3LYP potential function for rotation about the C2–Se9 bond. The values of the H6–C2–S9–H10 dihedral angle are given on the abscissa. This dihedral angle is 75.1° for *sc*, the MW spectrum of which was assigned in this work. The B3LYP and MP calculations predict that a second rotamer, *ap*, exists with a H6–C2–Se9–H10 dihedral angle of about 180°.

### Experimental Section

[CAUTION: Cyclopropaneselenol, which was prepared as described elsewhere,<sup>10</sup> is malodorous and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.] The spectrum of cyclopropaneselenol was recorded in the 21.9–80 GHz frequency interval by Stark-modulation spectroscopy, by using the MW 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 has been given elsewhere.<sup>15,16</sup> The spectra were recorded at room temperature or with the Stark cell cooled to about –20 °C with solid CO<sub>2</sub>, in an attempt to increase the intensity of the spectrum.

### Results and Discussion

**Quantum-Chemical Calculations.** The present ab initio and density functional theory (DFT) calculations were conducted by employing the Gaussian 03 suite of programs,<sup>17</sup> running on the 64 processor HP superdome computer in Oslo. Electron correlation was taken into consideration in the ab initio calculations by using Møller–Plesset second-order perturbation calculations (MP2).<sup>18</sup> Becke’s three-parameter hybrid functional<sup>19</sup> employing the Lee, Yang, and Parr correlation functional<sup>20</sup> (B3LYP) was employed in the DFT calculations. The 6-311++G(3df,3pd) basis set, which is of triple- $\zeta$  quality, includes polarization and diffuse functions, and is optimized for selenium,<sup>21</sup> was used throughout the calculations. The default convergence criteria of Gaussian 03 were employed.

Rotation about the C2–Se9 bond (see Figure 1) may produce rotational isomerism in this compound. B3LYP calculations were performed in an attempt to predict which rotameric forms are minima (stable conformers) of the potential-energy hypersurface. Calculations of energies were performed for the 0–180° interval in steps of 10° of the H6–C2–Se9–H10 dihedral angle by employing the scan option of the Gaussian 03 program and allowing all remaining structural parameters to vary freely. The resulting potential function, which is shown in Figure 2, has two minima close to 75 (*sc*) and 180° (*ap*) of the H6–C2–Se9–H10 dihedral angle and two maxima at about 0 and 150°.

Separate B3LYP calculations of the structures, energies, dipole moments, vibrational frequencies, Watson’s A-reduction

**TABLE 1: B3LYP and MP2 Geometries<sup>a,b</sup> of the *sc* and *ap* Conformers of C<sub>3</sub>H<sub>5</sub>SeH**

	B3LYP		MP2	
	<i>sc</i>	<i>ap</i>	<i>sc</i>	<i>ap</i>
Bond Length (pm)				
C1–C2	150.2	149.7	150.3	149.8
C1–C3	150.4	151.3	150.3	151.2
C1–H4	108.0	108.1	107.9	108.0
C1–H5	108.2	108.2	108.0	108.0
C2–C3	150.4	149.7	150.6	149.8
C2–H6	108.0	108.1	108.0	108.1
C2–Se9	194.2	195.0	191.6	192.5
C3–H7	108.1	108.2	107.9	108.0
C3–H8	108.1	108.1	108.0	108.0
Se9–H10	147.3	147.2	146.3	146.2
Angle (deg)				
C2–C1–H4	117.8	118.0	117.1	117.2
C2–C1–H5	117.2	118.1	116.9	117.9
C3–C1–H4	117.7	117.7	117.4	117.5
C3–C1–H5	118.4	118.7	118.0	118.1
H4–C1–H5	114.9	114.2	115.9	115.3
C1–C2–H6	117.7	117.5	117.3	117.4
C1–C2–Se9	121.2	123.2	120.2	121.8
C3–C2–H6	117.1	117.5	116.6	117.4
C3–C2–Se9	117.6	123.2	116.6	121.8
H6–C2–Se9	113.2	108.3	115.0	110.2
C1–C3–H7	118.8	118.6	118.3	118.1
C1–C3–H8	117.5	117.7	117.3	117.5
C2–C3–H7	117.4	118.1	117.2	117.9
C2–C3–H8	118.0	117.9	117.3	117.2
H7–C3–H8	114.6	114.3	115.6	115.3
C2–Se9–H10	96.1	95.0	95.7	93.7
Dihedral Angle (deg)				
H4–C1–C2–H6	–145.5	–144.8	–146.0	–144.9
H4–C1–C2–Se9	1.5	–5.2	2.4	–3.8
H5–C1–C2–H6	–1.8	–0.7	–1.9	–0.3
H5–C1–C2–Se9	145.2	138.9	146.5	140.9
H4–C1–C3–H7	145.4	144.6	146.2	145.4
H4–C1–C3–H8	0.2	–0.0	0.2	–0.0
H5–C1–C3–H7	–0.0	–0.0	–0.0	–0.0
H5–C1–C3–H8	–145.2	–144.6	–146.0	–145.4
H6–C2–C3–H7	1.1	0.7	0.9	0.3
H6–C2–C3–H8	144.8	144.9	145.1	144.9
Se9–C2–C3–H7	–139.0	–139.0	–140.4	–140.9
Se9–C2–C3–H8	4.7	5.1	3.8	3.8
C1–C2–Se9–H10	–73.3	35.1	–72.1	36.4
C3–C2–Se9–H10	–143.3	–39.2	–141.2	–36.5
H6–C2–Se9–H10	75.1	177.9	76.9	180.0

<sup>a</sup> Basis set: 6-311++G(3df,3pd). <sup>b</sup> Atom numbering is given in Figure 1.

centrifugal distortion constants,<sup>22</sup> and vibration–rotation constants (the  $\alpha$ 's)<sup>23</sup> were then performed for *sc* and *ap*. The starting values of the H6–C2–Se9–H10 dihedral angles were chosen to be close to 75 and 180°, respectively. Full geometry optimizations with no symmetry restrictions were undertaken. The H6–C2–Se9–H10 dihedral angle was found to be 75.1° for *sc* and 177.9° for *ap*. Only positive values were found for the harmonic vibrational frequencies of each of these conformers, as expected for minima on the potential-energy hypersurface. The B3LYP structures of *sc* and *ap* found in these calculations are listed in Table 1, and parameters of spectroscopic interest are listed in Table 2.

The electronic energy difference between the two rotamers was predicted to be 8.08 kJ/mol, with *sc* as the more stable rotameric form. This energy difference becomes 7.26 kJ/mol when the effect of the harmonic zero-point vibrational energy

**TABLE 2: B3LYP<sup>a</sup> and MP2<sup>a</sup> Parameters<sup>b</sup> of Spectroscopic Interest of C<sub>3</sub>H<sub>5</sub><sup>80</sup>SeH**

	B3LYP		MP2		experimental <sup>c</sup>
	<i>sc</i>	<i>ap</i>	<i>sc</i>	<i>ap</i>	<i>sc</i>
Rotational Constants (MHz)					
<i>A</i>	15490.8	15745.1	15458.9	15692.0	15308.406(11)
<i>B</i>	2485.0	2396.3	2547.8	2461.9	2531.31924(94)
<i>C</i>	2353.8	2305.4	2412.9	2369.2	2396.75503(94)
Quartic Centrifugal Distortion Constants <sup>c</sup> (kHz)					
$\Delta_J$	0.643	0.562	0.639	0.577	0.6683(26)
$\Delta_{JK}$	0.412	0.800	0.321	0.656	0.320(12)
$\Delta_K$	16.7	17.1	16.0	16.5	12.2(10)
$\delta_J$	0.0189	0.00994	0.0180	0.00928	0.018806(63)
$\delta_K$	0.865	-7.71	0.799	-8.36	0.924(48)
Dipole Moments <sup>d</sup> (10 <sup>-30</sup> C m)					
$\mu_a$	4.5	5.0	4.9	5.5	
$\mu_b$	1.7	0.1	2.0	0.0	
$\mu_c$	1.2	0.3	1.3	0.4	
$\mu_{\text{tot}}$	5.0	5.0	5.5	5.5	
Energy Differences <sup>e</sup> (kJ/mol)					
$\Delta E$	0.0 <sup>f</sup>	7.3	0.0	7.9 <sup>g</sup>	

<sup>a</sup> Basis set: 6-311++G(3df, 3pd). <sup>b</sup> A-reduction.<sup>17</sup> <sup>c</sup> O<sup>+</sup>-state. <sup>d</sup> 1 debye = 3.33564 × 10<sup>-30</sup> C m. <sup>e</sup> Corrected for zero-point vibrational energy. <sup>f</sup> Electronic energy: -1355 196.34 kJ/mol. <sup>g</sup> Electronic energy: -1353 046.16 kJ/mol.

is taken into consideration. The latter value for the energy difference is listed in Table 2.

The two maxima of the potential function were explored next by using the transition-state option of Gaussian 03. The first transition state was found for a value of exactly 0° of the H6–C2–Se9–H10 dihedral angle and an electronic energy that is 10.94 kJ/mol higher than the electronic energy of *sc*. The second transition state was found at 157.7° (8.30 kJ/mol above the energy of *sc*). Each of these maxima has one imaginary vibrational frequency associated with the torsion about the C2–S9 bond, which indicates that they are first-order transition states. The full potential function for rotation about the C2–Se9 bond not corrected for zero-point energies could now be constructed, as shown in Figure 2. Projections of the B3LYP structure in the principal inertial axes system in the case of the parent <sup>80</sup>Se isotopologue is shown in Figure 3.

MP2/6-311++G(3df,3pd) calculations of the energies, structures, dipole moments, harmonic vibrational frequencies, and quartic centrifugal distortion constants were repeated for *sc* and *ap*, because we wanted to compare the results obtained by the B3LYP and MP2 methods with each other as well as with the experimental results. Selected MP2 results are therefore included in Tables 1 and 2.

It is seen from Table 2 that the MP2 energy difference corrected for zero-point vibrational effects was predicted to be 7.89 kJ/mol, with *sc* as the more stable, close to the B3LYP result (7.26 kJ/mol). H6–C2–Se9–H10 dihedral angle of *sc* was predicted to be 76.3°, slightly larger than the B3LYP result (75.1), whereas the value of this angle was calculated to be exactly 180° for *ap*, compared to 177.9° found in the B3LYP calculations. However, it is seen from Figure 2 that the region around 180° of the B3LYP potential function is almost flat.

Both theoretical methods predict the C–H bond lengths (Table 1) to be 107.9–108.2 pm compared to the experimental equilibrium distance of 107.42(29) pm found in cyclopropane.<sup>24</sup> The three C–C bond lengths in *sc* are predicted to be 149.7–151.3 pm, similar to the equilibrium bond length of 151.01(23) pm in cyclopropane.<sup>24</sup> Interestingly, although the

three C–C distances in *sc* are found to be very similar in the calculations (Table 1), this is not the case for *ap*. In this conformer, the C1–C3 bond, which is opposite to the Se9H10 substituent, is approximately 1.5 pm longer than the C1–C2 and C1–C3 bonds, which is adjacent to the selenol group. This difference between the lengths of the carbon bonds of a substituted cyclopropane with C<sub>s</sub> symmetry is typical.<sup>25</sup>

Moreover, it is seen from Table 1 that the B3LYP C2–Se9 bond lengths are longer than the MP2 counterparts by about 2.5 pm and that Se9–H10 bond lengths are roughly 1 pm longer in the B3LYP calculations. The experimental *r*<sub>0</sub> Se–H bond length in CH<sub>3</sub>SeH is 147.3(16) pm, whereas the corresponding *r*<sub>s</sub> bond length is 144.0(10) pm in the antiperiplanar form and 146.7(4) pm in the synclinal conformer of ethaneselenol,<sup>14</sup> which is fairly close to the theoretical predictions (Table 1).

It is also noted that bond angles and dihedral angles found in the two procedures generally agree to within about 2° and that there is satisfactory agreement between the theoretical quartic centrifugal distortion constants, dipole moments, and energy differences (Table 2).

**MW Spectrum and Assignment of the Ground Vibrational State of the C<sub>3</sub>H<sub>5</sub><sup>80</sup>SeH Isotopologue.** The quantum chemical calculations above strongly indicate that *sc* is preferred over *ap*. This rotamer is a very prolate rotor (Ray's asymmetry parameter<sup>26</sup>  $\kappa \approx -0.98$ ) and has its major dipole-moment component along the *a*-inertial axis, with lesser components along the *b*- and *c*-inertial axes (Table 2). Selenium has six naturally occurring isotopes, of which five are relatively abundant (<sup>76</sup>Se (9.0%), <sup>77</sup>Se (7.6%), <sup>78</sup>Se (23.5%), <sup>80</sup>Se (49.8%), and <sup>82</sup>Se (9.2%)).

$\mu_b$  is antisymmetrical with respect to the torsion of the selenol group, as can be seen from Figure 3, and *b*-type rotational transitions therefore connect energy levels in torsional states of opposite parity and will depend strongly on the energy of the separation,  $\Delta$ , of these states. The selection rules of the *b*-type lines are therefore those of a rigid rotor plus (+)  $\leftarrow$  (–) or (–)  $\leftarrow$  (+), whereas the *a*- and *c*-type transitions occur between states of the same parity and will therefore depend little on  $\Delta$ . The present quantum chemical calculations are not sufficiently accurate to allow a quantitative prediction of  $\Delta$ ; therefore, no indication of its value was available from the theoretical calculations.

The spectrum is fairly dense and of moderate intensity. A search for <sup>a</sup>*R*-transitions of the spectrum of the most abundant <sup>80</sup>Se isotopologue was first performed by using the B3LYP spectroscopic constants (Table 2) to predict the approximate frequencies of these transitions, which were readily assigned. The preliminary spectroscopic constants obtained from these lines were used to predict the frequencies of *b*- and *c*-type *Q*-branch transitions, which involved intermediate values of the *J* principal quantum number. These transitions were expected to be significantly weaker than the <sup>a</sup>*R*-lines because  $\mu_a \approx 2.5 \times \mu_b$  and  $\mu_a \approx 3.5 \times \mu_c$  according to the theoretical predictions (Table 2). The *b*- and *c*-type *Q*-branch lines were generally found within a few megahertz from the predicted frequencies. Additional transitions involving higher values of *J* were successively included in the fit. Lines with a maximum of *J* = 58 were ultimately assigned in this manner.

All the *b*-type lines were split by roughly 1.4 MHz, corresponding to 2 ×  $\Delta$ , whereas no resolved splittings were seen for the <sup>a</sup>*R*- and <sup>c</sup>*Q*-lines. It was therefore assumed that the tunneling frequency is about 0.7 MHz.

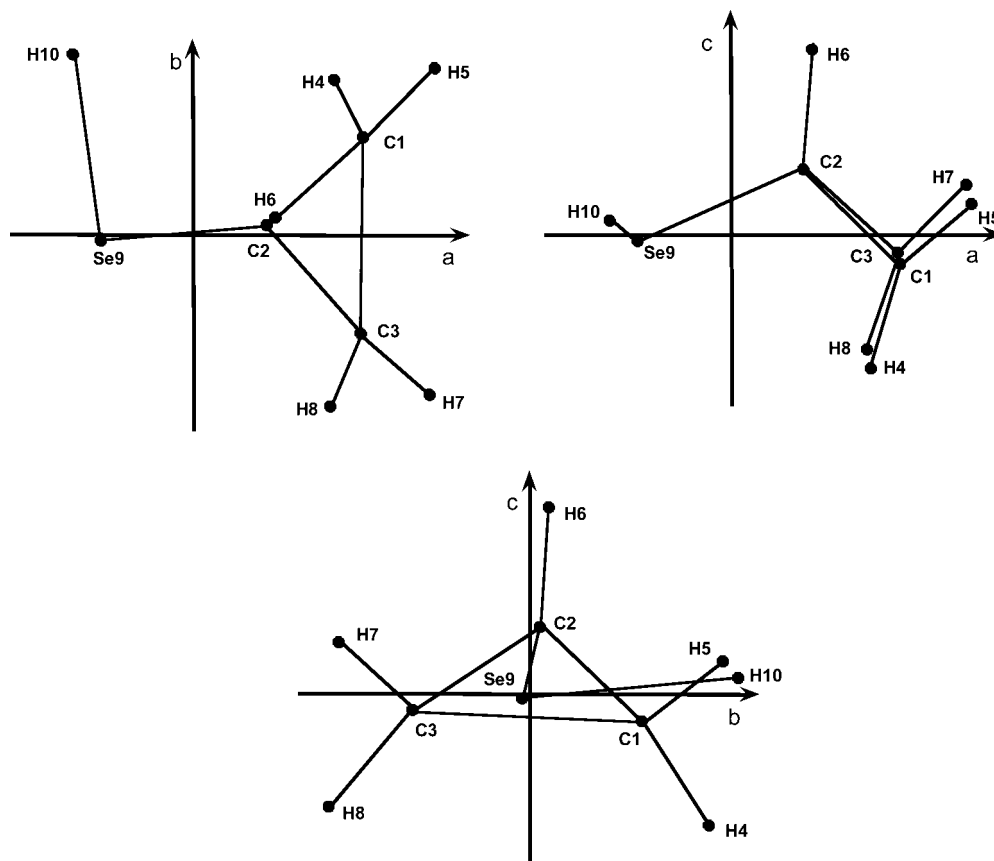


Figure 3. Projection of *sc* in the *a*–*b*, *a*–*c*, and *b*–*c* principal inertial axis planes.

A computer program, Asmix, by Nielsen,<sup>27</sup> deals with spectra of this type. This program is based on the reduced Hamiltonian defined as follows:<sup>27</sup>

$$H_{\text{red}} = |0\rangle \{H_r^{(0)} + H_d^{(0)}\} \langle 0| + |1\rangle \{H_r^{(1)} + H_d^{(1)} + W_{01}\} \langle 1| + |0\rangle H_c \langle 1| + |1\rangle H_c \langle 0|$$

where the label 0 corresponds to the (+) state and the label 1 corresponds to the (–) state.

By using *I'* representation,<sup>23</sup> one has

$$H_r(\nu) = B^{(\nu)} J_b^2 + C^{(\nu)} J_c^2 + A^{(\nu)} J_a^2$$

where  $\nu$  refers to the (+) or the (–) state, respectively.

$H_d = \{\text{Watson}^{30} \text{ quartic and sextic centrifugal distortion constants}\}^{(\nu)}$

$$W_{01} = \langle 1|H_{\text{vib}}|0\rangle - \langle 0|H_{\text{vib}}|1\rangle$$

$W_{01}$  corresponds to  $\Delta$  above.

$H_c$  is the coupling term of the form

$$H_c = \mu_{ij} \langle J_i J_j + J_j J_i \rangle$$

where *i* and *j* refer to the principal inertial axis.  $\mu_{ij}$  is the reduced moment of inertia.

A total of 448 transitions, which are listed in Table 1S in the Supporting Information, were used to determine the spectroscopic constants shown in Table 3. The effect of centrifugal distortion is not very prominent in this spectrum, and only quartic centrifugal distortion constants were therefore included in the least-squares fit. The rotational and quartic centrifugal distortion constants were varied in the least-squares fit together with the tunneling frequency  $\Delta$ . Attempts to determine the  $\mu_{ij}$  coupling constants failed, presumably because

of the rather small energy difference between the (+)- and (–)-tunneling states. The root-mean-square deviation of the fit was 0.132 MHz, a bit more than the experimental uncertainty of  $\pm 0.10$  MHz. The tunneling frequency,  $\Delta$ , was determined to be 0.693(55) MHz. The *B* and *C* rotational constants (Table 3) of the  $0^+$  and  $0^-$  substates are the same within the stated uncertainties, whereas a minor, but significant, difference is seen for the *A* rotational constants of the two states.

A prediction of  $\Delta$  is not given by the Gaussian program, and an estimate of its value was therefore performed as follows, by using the potential curve shown in Figure 2, which was least-squares fitted to the expression  $V(\phi) = \sum (1/2)V_i(1 - \cos(i\phi))$ . The five first terms of this expansion were retained, and they were found to be  $V_1 = 112.4(9)$ ,  $V_2 = -724.8(8)$ ,  $V_3 = -339.4(9)$ ,  $V_4 = 29.8(9)$ , and  $V_5 = -15.3(9)$   $\text{cm}^{-1}$ . Following Lewis et al.,<sup>28</sup> the energy levels, *E*, were calculated from  $-Bd^2\Psi/d\phi^2 + V(\phi) = E\Psi$ , by using a program by Bjørseth.<sup>29</sup> The value of *B* of the <sup>80</sup>Se isotopologue was calculated from the B3LYP structure as described by Pitzer and Gwinn<sup>30</sup> to be 7.896  $\text{cm}^{-1}$ . In this manner,  $\Delta$  was estimated to be 0.79 MHz, in excellent agreement with the experimental value of 0.693(55) MHz. Similarly, the C2–Se9 torsional frequency was estimated to be 178  $\text{cm}^{-1}$ , compared to the B3LYP value of 172  $\text{cm}^{-1}$ .

The tunneling frequency of 0.693(55) MHz is much smaller than 4115.26(42) MHz in the oxygen analogue ( $\text{C}_3\text{H}_5\text{OH}$ )<sup>1</sup> but similar to 1.664(22) MHz found for  $\text{C}_3\text{H}_5\text{SH}$ .<sup>6</sup> A large decrease in the tunneling frequency upon going from alcohols to thiols or selenols seems to be typical, whereas selenols and thiols seem to have rather similar  $\Delta$ 's. For example, in the synclinal conformer of  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\Delta$  is 97734.3 MHz,<sup>31</sup> whereas in the similar rotamer of  $\text{CH}_3\text{CH}_2\text{SH}$ , a value of 1753.84(29) has



**TABLE 3: Spectroscopic Constants<sup>a,b</sup> of the Ground Vibrational State of the *sc* Conformer of the C<sub>3</sub>H<sub>5</sub><sup>80</sup>SeH and C<sub>3</sub>H<sub>5</sub><sup>78</sup>SeH Isotopologues<sup>c</sup>**

	C <sub>3</sub> H <sub>5</sub> <sup>80</sup> SeH		C <sub>3</sub> H <sub>5</sub> <sup>78</sup> SeH	
	(+)	(-)	(+)	(-)
<i>A</i> (MHz)	15308.406(11)	15308.381(11)	15310.107(15)	15310.097(15)
<i>B</i> (MHz)	2531.31923(94)	2531.31919(94)	2550.30027(78)	2550.30052(78)
<i>C</i> (MHz)	2396.75503(94)	2396.75484(94)	2413.74133(77)	2413.74116(77)
$\Delta_J$ (kHz)	0.6683(26)	0.6683(22)	0.6596(20)	0.6594(20)
$\Delta_{JK}$ (kHz)	0.320(12)	0.321(12)	0.3989(84)	0.4000(84)
$\Delta_K$ (kHz)	12.2(10)	11.0(10)	10.4(14)	10.0(14)
$\delta_J$ (kHz)	0.018806(63)	0.018797(63)	0.01938(11)	0.01955(11)
$\delta_K$ (kHz)	0.924(48)	0.937(46)	0.999(49)	0.944(49)
$\Delta^d$ (MHz)		0.693(55)		0.608(71)
rms <sup>e</sup> (MHz)		0.132		0.096
no. of transitions in fit		448		324
maximum value of <i>J</i>		58		40

<sup>a</sup> As defined by Nielsen.<sup>27</sup> <sup>b</sup> Uncertainties represent one standard deviation. <sup>c</sup> The full spectra are given in Tables 1S and 2S in the Supporting Information. <sup>d</sup>  $\Delta = W_{01}$  (energy separation between tunneling states).<sup>27</sup> <sup>e</sup> Root-mean-square deviation. Unit weights were assumed for the transitions used in the fit.

been<sup>32</sup> reported compared to 1083.33(4) MHz in synclinal C<sub>3</sub>H<sub>5</sub>CH<sub>2</sub>SeH.<sup>14</sup>

The rotational and centrifugal distortion constants of the 0<sup>+</sup> state of this isotopologue are also listed in Table 2 for convenient comparison with the calculated values. The B3LYP rotational constants deviate from the experimental rotational constants by 1.2, -1.8, and -1.8% in the cases of *A*, *B*, and *C*, respectively, as can be seen from this table. The corresponding MP2 rotational constants deviate by 1.0, 0.7, and 0.7%, respectively. The theoretical B3LYP and MP2 rotational constants have been obtained from approximate equilibrium structures, whereas the experimental rotational constants reflect an effective *r*<sub>0</sub>-structure, which by definition is different from the equilibrium structure. However, the good agreement between the experimental and calculated rotational constants is an indication that the structure associated with the experimental rotational constants is close to the B3LYP and the MP2 structures. The MP2 rotational constants are slightly closer to the experimental counterparts than the B3LYP rotational constants are. Interestingly, MP2 structures obtained by using a large basis set are close to the true equilibrium structures.<sup>33</sup>

There is satisfactory agreement between the calculated and experimental quartic centrifugal distortion constants (Table 2). The quality of the B3LYP predictions seems to be about the same as that of the MP2 calculations, as can be seen from this table.

**Assignment of the Ground Vibrational State of Further Isotopologues.** The assignment of the spectrum of the C<sub>3</sub>H<sub>5</sub><sup>78</sup>SeH isotopologue (23.5% relative abundance) was straightforward. The spectrum, consisting of 324 transitions, is found in the Supporting Information, Table 2S, and the spectroscopic constants are listed in Table 2. The intensity of this spectrum is about half of that of the <sup>80</sup>Se isotopologue, as expected, but this did not prevent us from assigning the <sup>b</sup>*Q*-lines and thereby obtaining the tunneling frequency for this isotopologue as well.  $\Delta$  is 0.608(71) MHz (Table 3), slightly less than 0.693(55) MHz found above for the parent species.

A total of 107 *a*- and *b*-type transitions of the C<sub>3</sub>H<sub>5</sub><sup>82</sup>SeH species (9.2% relative abundance) was assigned, but we were not able to resolve the tunneling splitting of the <sup>b</sup>*Q*-branch lines, which were only seen to be broadened, in this case. The spectrum of this species is found in Table 3S in the Supporting Information. The spectroscopic constants reported in Table 4 were obtained by using a weighted least-squares fit of the

**TABLE 4: Spectroscopic Constants<sup>a,b</sup> of the Ground Vibrational State of the *sc* Conformer of the C<sub>3</sub>H<sub>5</sub><sup>82</sup>SeH, C<sub>3</sub>H<sub>5</sub><sup>76</sup>SeH, and C<sub>3</sub>H<sub>5</sub><sup>77</sup>SeH Isotopologues<sup>c</sup>**

	C <sub>3</sub> H <sub>5</sub> <sup>82</sup> SeH	C <sub>3</sub> H <sub>5</sub> <sup>76</sup> SeH	C <sub>3</sub> H <sub>5</sub> <sup>77</sup> SeH
<i>A</i> (MHz)	15307.072(63)	15311.9 <sup>d</sup>	15310.9 <sup>d</sup>
<i>B</i> (MHz)	2513.333(15)	2570.238(19)	2560.26(12)
<i>C</i> (MHz)	2380.390(16)	2431.534(21)	2422.36(12)
$\Delta_J$ (kHz)	0.6403(40)	0.6792(75)	0.618(42)
$\Delta_{JK}$ (kHz)	0.325(22)	0.380(30)	0.350(42)
$\Delta_K$ (kHz)	12.16 <sup>d</sup>	12.1 <sup>d</sup>	12.1 <sup>d</sup>
$\delta_J$ (kHz)	0.219(20)	0.031(34)	0.45(34)
$\delta_K$ (kHz)	0.92 <sup>d</sup>	0.92 <sup>d</sup>	0.92 <sup>d</sup>
rms <sup>e</sup> (MHz)	1.02	1.13	0.85
no. of transitions in fit	107	87	38
maximum value of <i>J</i>	22	14	12

<sup>a</sup> *A*-reduction *I*<sup>r</sup>-representation. <sup>b</sup> Uncertainties represent one standard deviation. <sup>c</sup> The full spectra are given in Tables 3S–5S in the Supporting Information. <sup>d</sup> Fixed. <sup>e</sup> Root-mean-square deviation of a weighted least-squares fit.

**TABLE 5: Spectroscopic Constants<sup>a,b</sup> of Vibrational Excited States of the *sc* Conformer of the C<sub>3</sub>H<sub>5</sub><sup>80</sup>SeH Isotopologue<sup>c</sup>**

	C–S torsion	lowest bending
<i>A</i> (MHz)	15306.754(57)	15265.796(57)
<i>B</i> (MHz)	2523.5348(92)	2528.997(14)
<i>C</i> (MHz)	2392.8962(89)	2393.306(14)
$\Delta_J$ (kHz)	0.6454(48)	0.6396(65)
$\Delta_{JK}$ (kHz)	0.448(23)	0.514(25)
$\Delta_K$ (kHz)	12.1 <sup>d</sup>	12.1 <sup>d</sup>
$\delta_J$ (kHz)	0.084(16)	0.209(13)
$\delta_K$ (kHz)	0.92 <sup>d</sup>	0.92 <sup>d</sup>
rms <sup>e</sup> (MHz)	1.21	1.35
no. of transitions in fit	105	76
maximum value of <i>J</i>	21	24

<sup>a</sup> *A*-reduction *I*<sup>r</sup>-representation. <sup>b</sup> Uncertainties represent one standard deviation. <sup>c</sup> The full spectra are given in Tables 6S and 7S in the Supporting Information. <sup>d</sup> Fixed. <sup>e</sup> Root-mean-square deviation of a weighted least-squares fit.

transitions reported in Table 3S in the Supporting Information. Sørensen's program ROTFIT<sup>34</sup> was employed for this purpose.

The spectroscopic constants of this species listed in Table 4, where it is noted that two of the centrifugal distortion constants ( $\Delta_K$  and  $\delta_K$ ) were held fixed at values obtained for the (+)-state of the parent (<sup>80</sup>Se) species (Tables 2 and 3), because the selection of assigned lines was not sufficient to allow an accurate determination of these two constants.

**TABLE 6: Spectroscopic Constants<sup>a,b</sup> of Vibrational Excited States of the *sc* Conformer of the C<sub>3</sub>H<sub>5</sub><sup>78</sup>SeH Isotopologue<sup>c</sup>**

	C–S torsion	lowest bending
A (MHz)	15308.3 <sup>d</sup>	15267.3 <sup>d</sup>
B (MHz)	2542.4221(94)	2547.899(14)
C (MHz)	2409.915(10)	2410.286(15)
$\Delta_J$ (kHz)	0.6805(54)	0.6643(63)
$\Delta_{JK}$ (kHz)	0.287(19)	0.475(41)
$\Delta_K$ (kHz)	10.4 <sup>d</sup>	10.4 <sup>d</sup>
$\delta_J$ (kHz)	0.02 <sup>d</sup>	0.02 <sup>d</sup>
$\delta_K$ (kHz)	1.0 <sup>d</sup>	1.0 <sup>d</sup>
rms <sup>e</sup> (MHz)	1.45	1.32
no. of transitions in fit	99	71
maximum value of <i>J</i>	21	24

<sup>a</sup> A-reduction *P*-representation. <sup>b</sup> Uncertainties represent one standard deviation. <sup>c</sup> The full spectra are given in Tables 8S and 9S in the Supporting Information. <sup>d</sup> Fixed. <sup>e</sup> Root-mean-square deviation of a weighted least-squares fit.

A total of 87 <sup>a</sup>*R*-lines, which are listed in Table 4S in the Supporting Information, was assigned for the C<sub>3</sub>H<sub>5</sub><sup>76</sup>SeH isotopologue (9.0% relative abundance). An accurate value for the *A* rotational constant cannot be obtained from this selection of transitions, because this compound is nearly completely prolate. The *A* rotational constant shown in Table 4 was therefore held fixed in the least-squares fitting procedure. This rotational constant was estimated as follows. The B3LYP structure of the <sup>80</sup>Se and <sup>76</sup>Se isotopologues were used to calculate the shift in the *A* rotational constant upon isotopic substitution. This shift was added to the experimental *A* rotational constant of the (+)-species of the <sup>80</sup>Se isotopologue (Tables 2 and 3). In this manner, the value of *A* for the <sup>76</sup>Se species was estimated to be 15311.9 MHz, as reported in Table 4.

Finally, 45 <sup>a</sup>*R*-lines of the MW spectrum of the C<sub>3</sub>H<sub>5</sub><sup>77</sup>SeH isotopologue (7.6% relative abundance) were assigned (Table 5S in the Supporting Information), and the rotational constants are shown in Table 4. The *A* rotational constants, which was held fixed in the fitting procedure, was estimated in the same manner as that described for the <sup>76</sup>Se species.

**Vibrationally Excited States.** The three lowest vibrational fundamentals of *sc* corrected for anharmonicity (not given in Tables 1 or 2) were predicted at  $\nu_{24} = 172$ ,  $\nu_{23} = 256$ , and  $\nu_{22} = 281$  cm<sup>-1</sup>, according to the B3LYP calculations.  $\nu_{24}$  is the torsion about the C2–Se9 bond, whereas  $\nu_{23}$  and  $\nu_{22}$  are the two lowest bending vibrations. The spectra of these three states should therefore have sufficient intensity to allow their assignments. The next fundamental frequency is predicted to occur at 547 cm<sup>-1</sup> according to the B3LYP calculations, and its MW spectrum would therefore have a very low intensity compared to the intensity of the ground-state spectrum.

The spectra of the first excited state of  $\nu_{24}$  and of  $\nu_{23}$  of the <sup>80</sup>Se and <sup>78</sup>Se species were indeed assigned and are listed in the Supporting Information, Tables 6S–9S. The spectrum of the first excited state of  $\nu_{22}$  of these two isotopic species was not found. The spectroscopic constants obtained from 105, 76, 99, and 71 transitions are reported in Tables 5 and 6. <sup>b</sup>*Q*-lines were assigned for  $\nu_{24}$  and  $\nu_{23}$ , but no resolution into the (+)- and (–)-components were seen for these transitions.

Rough relative intensity comparisons of the spectra of the ground-state and of the vibrationally excited states were performed for the <sup>80</sup>Se-species to determine the fundamental vibrational frequencies of these two excited states. The results were 178(40) for  $\nu_{24}$  and 210(40) cm<sup>-1</sup> for  $\nu_{23}$  compared to the B3LYP harmonic values of 172 and 256 cm<sup>-1</sup>, as stated above.

The MP2 values for these two fundamentals were 199 and 266 cm<sup>-1</sup>, respectively.

The experimental vibration–rotation constants (the  $\alpha$ 's) shown in the next paragraph for the <sup>80</sup>Se-isotopologue were calculated from  $\alpha_X = X_0 - X_1$ ,<sup>23</sup> where *X*<sub>0</sub> is the average of the (+)- and (–)-values of the *A*, *B*, or *C* rotational constants of the ground vibrational state (Table 3) and *X*<sub>1</sub> is the value of the rotational constants of the first excited state (Table 5).

The vibration–rotation constants of the  $\nu_{24}$  fundamental obtained in this manner were  $\alpha_A = 1.64$ ,  $\alpha_B = 7.79$ , and  $\alpha_C = 3.86$  MHz, compared to the B3LYP result (not given in Tables 1 or 2) of 1.85, 11.40, and 9.53 MHz, respectively. The experimental values of the  $\nu_{23}$  state are  $\alpha_A = 42.59$ ,  $\alpha_B = 2.32$ , and  $\alpha_C = 3.45$  MHz compared to the theoretical values of 42.88, 1.86, and 3.08 MHz, respectively. It can be concluded that there is satisfactory agreement between the experimental vibrational frequencies and the vibration–rotation constants and their B3LYP counterparts.

The assignments described in this section and in the previous section comprise all the strong lines of the spectrum as well as many weak ones. There is no indication of substantial amounts of a second form such as *ap*. This is in agreement with the theoretical calculations (Table 2), which predict an energy difference of ~8 kJ/mol between *ap* and *sc*. An energy difference of this size would result in a very small gas-phase fraction of *ap*, in accordance with the present findings.

## Conclusions

The MW spectra of five isotopologues of cyclopropaneselenol have been assigned and shown to belong to a conformation that has a synclinal orientation of the H–Se–C–H chain of atoms. The corresponding dihedral angle is ~75° from synperiplanar (0°), according to B3LYP/6–311++G(3df,3pd) and MP2/6–311++G(3df,3pd) calculations. There is no indication in the spectrum of substantial amounts of further rotameric forms.

The *b*-type transitions of the ground state of C<sub>3</sub>H<sub>5</sub><sup>80</sup>SeH and C<sub>3</sub>H<sub>5</sub><sup>78</sup>SeH were found to be split into two components. This splitting is assumed to be caused by tunneling between two equivalent synclinal potential wells. The tunneling frequency of the ground vibrational state of C<sub>3</sub>H<sub>5</sub><sup>80</sup>SeH is 0.693(55) MHz, whereas this frequency is 0.608(71) MHz for C<sub>3</sub>H<sub>5</sub><sup>78</sup>SeH. These values are much less than the tunneling frequency of the oxygen analogue, C<sub>3</sub>H<sub>5</sub>OH,<sup>1</sup> which has a tunneling frequency of 4115.26(42) MHz. Interestingly, the synclinal form of the sulfur counterpart, C<sub>3</sub>H<sub>5</sub>SH,<sup>6</sup> has a tunneling frequency of 1.664(22) MHz, which is similar to present findings for cyclopropaneselenol.

The two lowest vibrationally excited states were assigned for the <sup>80</sup>Se- and <sup>78</sup>Se-species, and their frequencies were determined by relative intensity measurements and found to be in satisfactory agreement with the calculated vibrational frequencies.

The B3LYP and MP2 methods predict structures that are in good agreement with each other. The rotational constants calculated from the B3LYP structures deviate by a maximum of 1.8% from the experimental values, whereas the theoretical MP2 constants deviate by no more than 1.0%, which indicates that the B3LYP and MP2 *r<sub>e</sub>*-structures are close to the *r<sub>0</sub>*-structure associated with the experimental rotational constants. The theoretical quartic centrifugal distortion constants and rotation–vibration constants of the two lowest vibrational fundamentals are in satisfactory agreement with their experimental counterparts.

**Acknowledgment.** We thank Anne Horn for her skilful assistance and Stig Rune Sellevåg for fitting the potential

function to the cosine expression. The Research Council of Norway (Program for Supercomputing) is thanked for a grant of computer time. R.M. thanks the Research Council of Norway for financial assistance through Contract 177540/V30. J.-C.G. thanks the University of Oslo for a travel grant and the National Program PCMI (INSU-CNRS) for financial support.

**Supporting Information Available:** The MW spectra of five isotopologues of cyclopropaneselenol are given in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Macdonald, J. N.; Norbury, D.; Sheridan, J. *J. Chem. Soc., Faraday Trans.* **1978**, 74, 1365.
- (2) Chaplinski, V.; Marstokk, K. M.; de Meijere, A.; Møllendal, H. *Acta Chem. Scand.* **1996**, 50, 486.
- (3) Leonov, A.; Marstokk, K.-M.; de Meijere, A.; Møllendal, H. *J. Phys. Chem. A* **2000**, 104, 4421.
- (4) Mochel, A. R.; Britt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1973**, 58, 3221.
- (5) Penn, R. E.; Boggs, J. E. *J. Chem. Phys.* **1973**, 59, 4208.
- (6) Mokso, R.; Møllendal, H.; Guillemin, J.-C. *J. Phys. Chem. A* **2008**, 112, 4601.
- (7) Penn, R. E.; Grossmann, R. W. *J. Mol. Spectrosc.* **1975**, 58, 333.
- (8) Bajor, G.; Veszprémi, T.; Riague, E. H.; Guillemin, J.-C. *Chem.-Eur. J.* **2004**, 10, 3649.
- (9) Guillemin, J.-C.; Bajor, G.; Riague, E. H.; Khater, B.; Veszprémi, T. *Organometallics* **2007**, 26, 2507.
- (10) Khater, B.; Guillemin, J.-C.; Bajor, G.; Veszprémi, T. *Inorg. Chem.* **2008**, 47, 1502.
- (11) Petitprez, D.; Demaison, J.; Wlodarczak, G.; Guillemin, J.-C.; Møllendal, H. *J. Phys. Chem. A* **2004**, 108, 1403.
- (12) Cole, G. C.; Møllendal, H.; Guillemin, J.-C. *J. Phys. Chem. A* **2006**, 110, 2134.
- (13) Møllendal, H.; Mokso, R.; Guillemin, J.-C. *J. Phys. Chem. A* **2008**, 112, 3053.
- (14) Nakagawa, J.; Okutani, H.; Hayashi, M. *J. Mol. Spectrosc.* **1982**, 94, 410.
- (15) Møllendal, H.; Leonov, A.; de Meijere, A. *J. Phys. Chem. A* **2005**, 109, 6344.
- (16) Møllendal, H.; Cole, G. C.; Guillemin, J.-C. *J. Phys. Chem. A* **2006**, 110, 921.
- (17) 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.; Bakken, V.; 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.: Wallingford, CT, 2004.
- (18) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, 46, 618.
- (19) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098.
- (20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
- (21) Curtiss, L. A.; McGrath, M. P.; Blaudreau, J.-P.; Davis, N. E.; Binning, R. C., Jr.; Radom, L. *J. Chem. Phys.* **1995**, 103, 6104.
- (22) Watson, J. K. G. *Vibrational Spectra and Structure*; Elsevier: Amsterdam, 1977; Vol. 6.
- (23) Gordy, W.; Cook, R. L. *Techniques of Chemistry*, Vol. XVII: *Microwave Molecular Spectra*; John Wiley & Sons: New York, 1984; Vol. XVII.
- (24) Endo, Y.; Chang, M. C.; Hirota, E. *J. Mol. Spectrosc.* **1987**, 126, 63.
- (25) Penn, R. E.; Boggs, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 666.
- (26) Ray, B. S. Z. *Physik* **1932**, 78, 74.
- (27) Nielsen, C. J. *Acta Chem. Scand., Ser. A* **1977**, A31, 791.
- (28) Lewis, J. D.; Malloy, T. B., Jr.; Chao, T. H.; Laane, J. J. *Mol. Struct.* **1972**, 12, 427.
- (29) Bjørseth, A. Personal communication, 1974.
- (30) Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* **1942**, 10, 428.
- (31) Kakar, R. K.; Quade, C. R. *J. Chem. Phys.* **1980**, 72, 4300.
- (32) Nakagawa, J.; Kuwada, K.; Hayashi, M. *Bull. Chem. Soc. Jpn.* **1976**, 49, 3420.
- (33) Helgaker, T.; Gauss, J.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1997**, 106, 6430.
- (34) Sørensen, G. O. *J. Mol. Spectrosc.* **1967**, 22, 325.

JP804137C