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Microwave and Quantum Chemical Study of Propargyl Selenocyanate ($HC\equiv CCH_2SeC\equiv N$)

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The microwave spectrum of propargyl selenocyanate ($HC\equiv CCH_2SeC\equiv N$) has been investigated in the 40−80 GHz spectral region at 0 °C. The spectra of the ground vibrational state of the ^{80}Se and ^{78}Se isotopologues of one conformer were assigned. The first vibrationally excited state of the torsion about the CC−Se bond was also assigned for the ^{80}Se isotopologue. The identified rotamer has a C−C−Se−C antiperiplanar conformation (C_s symmetry). The microwave work has been augmented by ab initio calculations at the MP2/6-311++(3df,3pd) level and density functional theory calculations at the B3LYP/6-311G++(3df,3pd) level of theory. Both the ab initio and the B3LYP calculations predict that the identified rotamer is the global minimum and indicate the existence of an additional high-energy anticlinal form. The two theoretical methods predict rather different values for the H_2C−Se bond length as well as for the C−C−Se−C dihedral angle of the high-energy anticlinal form.

Introduction

Few studies of the structural and conformational properties of organic selenocyanates (X−Se-C≡N) in the gaseous state have been performed. Several years ago, the microwave (MW) spectra of methyl (CH_3SeCN)[1,2] and ethyl selenocyanate (CH_3CH_2SeCN)[3] were investigated. The structure, dipole moment, and barrier to internal rotation of the methyl group were determined for CH_3SeCN,[1,2] whereas the conformational properties of CH_3CH_2SeCN were the theme of the other MW study.[3] The spectrum of only one rotamer, which has a synclinal (obsolete "gauche") conformation for the C−C−Se−C link of atoms, was identified in the latter case. The spectrum of the antiperiplanar ("trans") form of ethyl selenocyanate was not observable.

Recently, several new selenocyanates have been synthesized,[4−7] and this has made it possible to investigate the physical properties of additional members of this little-investigated family of compounds. In one such study, the MW spectrum of vinyl selenocyanate, $H_2C{=}CHSeCN$, was reported,[8] revealing the existence of two rotameric forms. The dihedral angle formed by the C═C−Se−C chain of atoms is 0° in the synperiplanar ("cis") conformer and takes the unusual value of 166(3)° in the second anticlinal ("skew") rotamer of this molecule.[8] The synperiplanar rotamer of $H_2C{=}CHSeCN$ is more stable than the anticlinal rotamer by 4.5(4) kJ/mol.[8] Very recently, the MW spectra of allenyl ($H_2C{=}C{=}CHSeCN$) and cyclopropyl selenocyanate (C_3H_5SeCN) were published.[9] One anticlinal conformer, which is the global minimum, was identified for $H_2C{=}C{=}CHSeCN$. The C═C−Se−C dihedral angle is 129(5)° in this rotamer. The hypothetical synclinal form of $H_2C{=}C{=}CHSeCN$, which is likely to be a high-energy form, was not assigned.[9] The conformational properties of vinyl ($H_2C{=}CHSeCN$)[8] and allenyl selenocyanate ($H_2C{=}C{=}CHSeCN$),[9] both of which have the selenocyanate group attached to a double-bonded carbon atom, are therefore remarkably different.

Cyclopropyl selenocyanate represents yet another conformational problem. In this case, a H−C−Se−C synclinal (80(4)° from synperiplanar) conformer was found to be the preferred.[9]

The conformational studies referred to above demonstrate that the selenocyanates have varied and interesting structural and conformational properties, which depend critically on the interaction between this group and neighboring functional groups. This first MW study of propargyl selenocyanate was undertaken because the interaction between the propargyl and the selenocyanate groups is different from the interactions in the selenocyanates already investigated by this technique[1−3,8,9] and discussed above. It should be mentioned that photoelectron spectra and quantum chemical calculations at the MP2/cc-pVTZ and B3LYP/cc-pVTZ levels of theory have already been reported for $HC\equiv CCH_2SeCN$, as well as for several other allenyl and alkynyl selenols and selenocyanates.[6]

The methods that we have used in this study are MW spectroscopy and high-level quantum chemical calculations. MW spectroscopy was chosen because of its extremely high accuracy and resolution, making this method especially suitable for conformational studies. The spectroscopic work has been augmented by high-level quantum chemical calculations, which were conducted with the purpose of obtaining information for the use in assigning the MW spectra and investigating properties of the potential energy hypersurface.

Experimental Section

Synthesis. *Propargyl selenocyanate is malodorous and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.*

The sample used in this experiment was synthesized and purified as described previously.[4]

Microwave Experiment. The MW spectrum was recorded in the 40−80 GHz spectral region using the Stark-modulated spectrometer of the University of Oslo. Details of the construction and operation of this spectrometer, which has a 2 m

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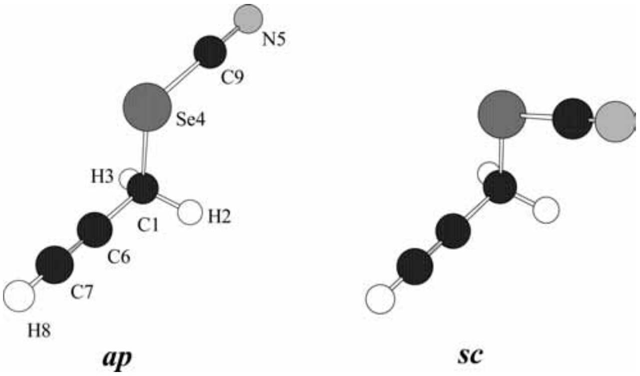

Figure 1. The antiperiplanar (**ap**) and synclinal (**sc**) rotamers of HC≡CCH$_2$SeCN. Atom numbering is shown on **ap**. The microwave spectrum of **ap** was assigned.

Hewlett−Packard Stark cell, have been given elsewhere.[10,11] The spectrum was taken with the cell cooled to roughly 0 °C. A reduction of the temperature from room temperature was done in order to enhance the intensity of the spectral lines. Lower temperatures, which would have increased the intensity of the spectra even more, could not be achieved, owing to insufficient vapor pressure. The spectral lines were found to be broad and were measured with an estimated accuracy of ≈±0.10 MHz for isolated lines. Radio frequency microwave double resonance experiments (RFMWDR), similar to those performed by Wodarczyk and Wilson,[12] were also conducted to assign unambiguously particular transitions.

Results

Quantum Chemical Calculations. The present ab initio and density functional theory (DFT) calculations were performed by employing the Gaussian 03 suite of programs,[13] running on the Titan cluster in Oslo. Electron correlation was taken into consideration in the ab initio calculations using Møller−Plesset second-order perturbation calculations (MP2).[14] Becke's three-parameter hybrid functional[15] employing the Lee, Yang, and Parr correlation functional[16] (B3LYP) was employed in the DFT calculations. The 6-311++G(3df,3pd) basis set was employed because this basis set has been optimized for selenium.

A model of this compound with atom numbering is shown in Figure 1. Rotation about the C1−Se4 bond may produce rotational isomerism. B3LYP calculations were performed in an attempt to predict which rotameric forms are minima ("stable") of the potential energy hypersurface. Calculations of energies were performed for the 0−180° interval in steps of 10° of the C6−C1−Se4−C9 dihedral angle, employing the scan option of the Gaussian 03 program, allowing all remaining structural parameters to vary freely. The synperiplanar (**sp**) conformation was assigned a value of 0° for this dihedral angle. The resulting potential function had two minima at 70 (synclinal) and ∼180° (antiperiplanar) of the C6−C1−Se4−C9 dihedral angle and maxima at 0 and ∼120°. The two "stable" conformers at 70 and 180° are henceforth denoted as **sc** and **ap.** They are sketched in Figure 1.

The two maxima of the potential function were explored next using the transition-state option of Gaussian 03. The first maximum was found for exactly 0° of the C6−C1−Se4−C9 dihedral angle with an electronic energy that was 11.49 kJ/mol higher than the energy of the global minimum **ap**. The second maximum was found at 116.9° (5.59 kJ/mol above the energy of **ap**). Each of these maxima has one imaginary vibrational frequency associated with the torsion about the C1−Se4 bond, which indicates that they are first-order transition states.

TABLE 1: MP2 and B3LYP Geometries[a] of the ap Conformer of H−C≡C−CH$_2$−SeC≡N

	method	
	MP2	B3LYP
	Bond Length (pm)	
C1−C2	108.7	108.6
C1−Se4	197.3	201.3
C1−C6	144.8	144.1
Se4−C9	183.5	184.3
N5−C9	117.6	115.5
C6−C7	121.4	119.9
C7−HH8	106.2	106.2
	Angle (deg)	
H2−C1−H3	110.2	110.2
H2−C1−Se4	107.7	106.8
H2−C1−C6	111.9	112.3
Se4−C1−C6	107.1	108.2
C1−Se4−C9	94.8	96.1
C6−C7−H8	179.0	179.3
C1−C6−C7	177.9	178.7
Se4−C9−N5	180.1	181.0
	Dihedral Angle (deg)	
H2−C1−Se4−C9	59.5	58.9
	Rotational Constant (MHz)[b]	
A	7815.5	7864.4
B	1293.2	1266.6
C	1117.4	1098.5
	Quartic Centrifugal Distortion Constant (kHz)[b]	
$\Delta_J{}^d$	0.168	0.159
$\Delta_{JK}{}^d$	−1.08	−0.927
$\Delta_K{}^d$	92.4	93.4
δ_J	0.0355	0.0323
δ_K	1.01	0.966
	Dipole Moment (10^{-30} C m)	
μ_a	14.1	13.8
μ_b	1.7	1.9
μ_c	0.0[c]	0.0[c]
	Δ^d (10^{-20} MHz u m^2)	
	3.18	3.20

[a] Basis set: 6-311++G(3df,3pd). [b] For the ^{80}Se isotopologue. [c] For symmetry reasons. [d] $\Delta = I_c - I_b - I_a$; where I_a, I_b, and I_c are the principal moments calculated using $I_a \times A = 505\,379.05 \times 10^{-20}$ MHz u m^2, and so forth.

Separate B3LYP calculations of the structures, energies, dipole moments, vibrational frequencies, Watson's *A* reduction centrifugal distortion constants,[17] and vibration−rotation constants (the α's)[18] were then undertaken for **ap** and **sc**. The starting values of the C6−C1−Se4−C9 dihedral angles were chosen to be close to 70 and 180°, respectively. Full geometry optimizations with no symmetry restrictions were made by employing the default convergence criteria of Gaussian 03. The C6−C1−Se4−C9 dihedral angle was found to be 70.4° in **sc** and exactly 180° in **ap,** which is therefore predicted to have a symmetry plane (C_s symmetry). Only positive values were found for the vibrational frequencies of each of the two conformers. The B3LYP parameters of **ap** are found in Table 1, and those of **sc** are listed in Table 2. The full electronic potential function for rotation about the C2−Se7 bond, which could now be drawn, is shown in Figure 2.

The electronic energy difference between the two rotamers was predicted to be 2.89 kJ/mol, with **ap** as the more stable form. This energy difference is not changed when the effects of the harmonic zero-point vibrational energies are taken into consideration. The B3LYP/cc-pVTZ energy difference has been reported to be practically the same (3.0 kJ/mol).[6]

TABLE 2: MP2 and B3LYP Geometries[a] of the sc Conformer of $H-C\equiv C-CH_2-SeC\equiv N$

	method	
	MP2	B3LYP
	Bond Length (pm)	
C1−C2	108.7	108.7
C1−Se4	197.3	200.9
C1−C6	144.5	143.9
Se4−C9	183.1	184.0
N5−C9	117.6	115.5
C6−C7	121.4	119.9
C7−H8	106.2	106.2
	Angle (deg)	
H2−C1−H3	109.0	108.8
H2−C1−Se4	107.4	106.4
H2−C1−C6	112.0	112.6
Se4−C1−C6	112.3	113.8
C1−Se4−C9	94.9	97.2
C6−C7−H8	179.9	179.8
C1−C6−C7	178.8	180.0
Se4−C9−N5	178.8	177.7
	Dihedral Angle (deg)	
H2−C1−Se4−C9	−63.6	−54.1
H3−C1−Se4−C9	−178.9	−168.3
C6−C1−Se4−C9	60.0	70.4
	Rotational Constant[b] (MHz)	
A	3170.8	3328.7
B	1950.9	1757.0
C	1310.2	1254.0
	Quartic Centrifugal Distortion Constant[b] (kHz)	
Δ_J	1.69	2.11
Δ_{JK}	7.41	−0.643
Δ_K	−7.80	7.05
δ_J	0.698	0.914
δ_K	6.91	6.04
	Dipole Moment (10^{-30} C m)	
μ_a	5.2	7.9
μ_b	13.1	11.5
μ_c	0.8	1.0

[a] Comments as those for Table 1. [b] Comments as those for Table 1.

MP2/6-311++G(3df,3pd) calculations of the structure, dipole moment, vibrational frequencies, and quartic centrifugal distortion constants were repeated for **sc** and **ap** because we wanted to compare results obtained by the MP2 procedure with the counterparts calculated by the B3LYP method, as well as with the relevant experimental findings. Selected MP2 results are therefore included in Tables 1 and 2.

While **ap** is found to have exact C_s symmetry in both the MP2 and in the B3LYP calculations, the MP2 C6−C1−Se4−C9 dihedral angle was predicted to be 60.0° in the **sc**, about 10° less than that found in the B3LYP calculations (70.4°). The finding that MP2 and B3LYP calculations both predict the existence of a conformer with exact C_s symmetry whereas deviations of 5−10° are found in the dihedral angles characterizing the second rotamer have also been seen for other selenocyanates such as $HC=CHSeCN$,[8] $H_2C=C=CHSeCN$,[9] and C_3H_5SeCN.[9] The $C\equiv C$ bond distances are typically 1.5 pm longer in MP2 than in the B3LYP calculations. The C−H bond lengths are practically the same in both methods. The C1−Se4 distances are approximately 4 pm longer in the B3LYP than in the MP2 calculations, whereas the B3LYP Se4−C9 bond lengths are longer by about 1 pm. There is also a significant difference in the predicted $C9\equiv N5$ bond length, which is ∼2 pm longer in the MP2 calculations. Bond angles calculated with the two procedures generally agree to within roughly 1°.

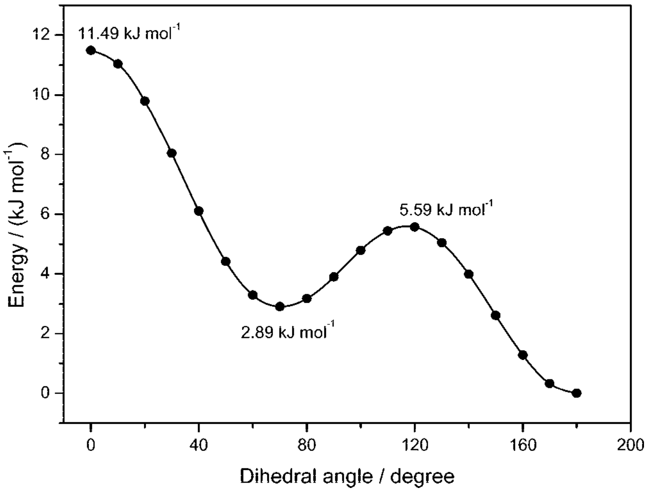

Figure 2. B3LYP/6-311++G(3df,3pd) electronic potential function for rotation about the C1−Se4 bond in $HC\equiv CCH_2SeCN$. The values of the C6−C1−Se4−C9 dihedral angle in degrees are given on the abscissa, and the relative energies in kJ/mol are given on the ordinate. Conformer **ap** has a C6−C1−Se4−C9 dihedral angle of exactly 180°. A dihedral angle of 70.4° is predicted for **sc**, which is calculated to be 2.89 kJ/mol less stable than the global minimum, **ap**. This potential function has maxima at exactly 0° (11.49 kJ/mol above the energy of **ap**) and at 116.9° (5.59 kJ/mol above the energy of **ap**).

Comparison with the substitution structure of H_3CSeCN[2] is warranted. The $Se-CH_3$ bond length, which is 194.4(7) pm in this compound, is about 3 pm shorter than the $Se-CH_2$ bond length obtained in MP2 calculations and as much as 6 pm shorter than the B3LYP procedure predicts. The Se−CN bond length is 183.6(11) pm in the methyl derivative,[2] which is similar to the MP2 and B3LYP calculations (Tables 1 and 2).

The MP2 energy difference corrected for zero-point vibrational effects was predicted to be 0.49 kJ/mol, with **ap** as the more stable conformer, similar to 1.0 kJ/mol found in the MP2/cc-pVTZ calculations.[6] The present B3LYP and MP2 results for the energy difference between the two forms therefore vary by 2.4 kJ/mol. There are also comparatively large deviations in the bond distances and bond angles associated with the Se atom. The rather long distance predicted for the $Se-CH_2$ bond compared to its counterpart in methyl selenocyanate is especially noteworthy. A significant deviation is also found for the C6−C1−Se4−C9 dihedral angle of **sc** (Table 2). All of this is not unexpected given the large number of electrons (68) involved in these calculations and the inherent approximations of the two methods of calculation.

Microwave Spectrum and Assignments for the ap Conformer. Survey spectra taken at about 0 °C revealed a comparatively weak and dense spectrum, with relatively broad absorption lines.

Several factors contribute to the intensity of a MW spectrum. The intensity is proportional to the square of the principal axis dipole moment components and inversely proportional to the partition function.[18] Conformer **ap** is predicted to possess a comparatively large μ_a and a very small μ_b, whereas μ_c is zero for symmetry reasons (Table 1). The hypothetical **sc** should have a large μ_b, a significant μ_a, and a small μ_c (Table 2). The fact that a relatively weak spectrum was observed must therefore indicate that the partition function is relatively large at 0 °C, which causes a low population in each quantum state and consequently a weak spectrum. The large value of this function is primarily caused by relatively small rotational constants (Tables 1 and 2) and several low-frequency vibrational fundamentals. The quantum chemical calculations above indicate that there is one fundamental below 50 cm^{-1} (the torsion about the C1−Se4 bond) and five to six additional fundamentals between 100 and 500 cm^{-1} (not given in Tables 1 or 2) both for **ap** and for **sc**.

Another factor that contributes negatively to the intensity is the fact that selenium has six naturally occurring isotopes, of which five are relatively abundant (^{76}Se (9.0%), ^{77}Se (7.6%), ^{78}Se (23.5%), ^{80}Se (49.8%), and ^{82}Se (9.2%)), which means that the intensity is reduced accordingly. The presence of relatively large concentrations of more than one rotameric form would have a similar effect on the intensity. Finally, the ^{14}N nucleus (99.6% abundance) has spin = 1, and nuclear quadrupole coupling effects will therefore split each transitions into several components, which were not resolved in our experiment but will broaden the lines and reduce peak intensities.

The theoretical predictions shown in Table 1 indicate that the parent ^{80}Se isotopologue of **ap** is a prolate asymmetrical top with Ray's asymmetry parameter[19] $\kappa \approx -0.95$. Pile-ups of ^{a}R branch transitions separated by roughly $B + C \approx 2.4$ GHz were expected in the 40−80 GHz spectral region. The high K_{-1} members of these series, which are practically degenerate, would be modulated at comparatively low Stark fields, and this would facilitate their assignments.

Series of crowded pile-ups were readily seen to protrude from the background of weaker transitions when a relatively low Stark field was applied. These pile-ups were the key to the assignment of the MW spectrum of **ap**. It was found that pairs of ^{a}R lines with identical $K_{-1} \geq 6$ coalesce in this spectral region because $\kappa \approx -0.95$ and that transitions with different values of K_{-1} frequently overlap. A total of 296 ^{a}R lines with $K_{-1} \geq 4$ were ultimately assigned. The assignment of several of these transitions was confirmed by RFMWDR experiments.[12] Definite assignments of lines with $K_{-1} < 4$ could not be made unambiguously primarily because these transitions have slow Stark effects and are therefore difficult to modulate, and they are often overlapped. The ^{a}R spectrum of **ap** was fitted to Watson's *A* reduction Hamiltonian using the I^r representation[17] employing Sørensen's program Rotfit.[20] The inverse squares of the estimated uncertainties of the transitions were used as weights in the least-squares fitting procedure. The spectrum is shown in Table 1S in the Supporting Information, and the spectroscopic constants are listed in Table 3.

It was impossible to determine the Δ_K, δ_J, and δ_K quartic centrifugal distortion constants for this near-prolate rotor from the assigned ^{a}R lines. These constants were therefore held fixed at the MP2 values (Table 2) in the least-squares fit. The *A* rotational constant (Table 3) also has a relatively large 1 standard deviation of 7.6 MHz. The value of Δ ($-3.26(10) \times 10^{-20}$ u m^2) defined by $\Delta = I_c - I_b - I_a$, where I_a, I_b, and I_c are the principal moments of inertia, is typical for a molecule with a symmetry plane and two sp^3-hybridized out-of-plane hydrogen atoms. Similar values are obtained in the theoretical calculations (Table 1).

The MW spectrum of the first excited state of the torsion about the C1−Se4 bond was assigned for the ^{80}Se species. The spectrum is listed in Table 2S in the Supporting Information, and the spectroscopic constants are displayed in Table 3. Rough relative intensity measurements yielded 58(30) cm^{-1} for the torsional vibration, compared to the harmonic values of 46 (B3LYP) and 45 cm^{-1} (MP2). The B3LYP anharmonic frequency was calculated to be 42 cm^{-1}.

The *A* rotational constant obtained from the transitions in Table 2S (Supporting Information) is very uncertain. A more accurate value of this constant can be estimated following Hanyu et al.,[21] using their eq 3 and assuming that the torsional frequency has the B3LYP value of 42 cm^{-1}. In this manner, one predicts the value of Δ in Table 3 to be approximately -4.9×10^{-20} u m^2, which was used to determine $A \approx 7755$ MHz. The vibration−rotation interaction constants (the α's)[18] defined by $\alpha_X = X_0 - X_1$, where X_0 are the ground-state rotational constants and X_1 are the rotational constants of a particular excited vibrational state, was found to be $\alpha_A = 123$, $\alpha_B = 0.0$, and $\alpha_C = -2.8$ MHz in the B3LYP calculations. These values are in good agreement with their counterparts (104, −0.4, and 2.3 MHz, respectively), which have been derived from the entries in Table 3.

TABLE 3: Spectroscopic Constants^{a,b} of the ap Conformer of $H-C\equiv C-CH_2-SeC\equiv N$

	$HC\equiv CCH_2{}^{80}SeCN$		$HC\equiv CCH_2{}^{78}SeCN$
	vibrational state		
species	ground	first ex. torsion	ground
A (MHz)	7859.4(76)	7755^{c}	7933.6^{c}
B (MHz)	1293.902(55)	1294.271(22)	1294.21(21)
C (kHz)	1119.017(55)	1121.256(25)	1121.06(20)
Δ_J (kHz)	0.17348(53)	0.1588(25)	0.158(16)
Δ_{JK} (kHz)	−1.0185(41)	−0.9852(63)	−1.010(67)
Δ_K (kHz)	93.4^{c}	93.4^{c}	93.4^{c}
δ_J (kHz)	0.0323^{c}	0.0323^{c}	0.0323^{c}
δ_K(kHz)	−0.993^{c}	−0.993^{c}	−0.993^{c}
Δ^{d} (10^{-20} u m^2)	−3.26(10)	−4.92(2)	−3.4(1)
rms^{e}	1.7444	1.3292	0.6799
no. of transitions^{f}	296	30	14

[a] *A* reduction, I^r representation.[17] Spectra are found in the Supporting Information, Tables 1S−3S. [b] Uncertainties represent one standard deviation. [c] Fixed; see text. [d] Δ is defined in the text. [e] Root-mean-square deviation. [f] Number of transitions used in the weighted least-squares fit.

The assignment of the ground-state spectrum of the ^{78}Se isotopologue was straightforward. The spectrum consisting of 14 transitions is listed in Table 3S in the Supporting Information, and the spectroscopic constants are given in Table 3. The *A* rotational constant was fixed at 7933.6 MHz in this case in order to reproduce Δ for ^{80}Se species, which must be almost the same as that for the ^{78}Se.

Attempts to assign the spectra of the ^{76}Se (9.0%) and ^{82}Se (9.2%) species were made, but these spectra were found to be so weak that a detailed assignment could not be achieved.

Structure of ap. It is of interest to compare the experimental rotational constants (Tables 3) of the ^{80}Se isotopologue with the theoretical counterparts (Table 1). The MP2 rotational constants *A*, *B*, and *C* deviate from the experimental rotational constants of the ground vibrational state by 0.8, 0.0, and 0.1%, respectively, whereas the B3LYP rotational constants differ by −0.1, 2.1, and 1.8%, respectively. The theoretical rotational constants are approximations of the equilibrium rotational constants, whereas the experimental rotational constants are effective constants. This makes a comparison somewhat difficult. However, an agreement to within 2%, or better, is expected. Both theoretical methods reproduce the rotational constants within this limit. It is therefore impossible to decide on this basis which computational procedure best approximates the equilibrium structure. However, the fact that the MP2 values of the Se−CH$_2$ distances are closer to the corresponding experimental value in methyl selenocyanate is perhaps an indication that the MP2 structure should be preferred. It has been pointed out that MP2 structures obtained using large basis sets are remarkably close to the equilibrium structure.[22]

Searches for sc. This rotamer is predicted to be less stable in both the MP2 and the B3LYP calculations. However, the statistical weight of **sc** is 2 compared to 1 for **ap**. The *b*-type spectrum of **sc** was expected to be much stronger than the *a*-type spectrum because μ_b is the predominating dipole moment component (Table 2). The *b*-type spectra are generally more difficult to assign than the *a*-type spectra. Extensive searches were made for both the *a*- and the *b*-type MW spectra of this form, but they were not found. It is concluded that it is likely that **sc** is a high-energy form of the molecule, in agreement with the theoretical predictions.

Conclusions

The microwave spectra of $HC\equiv CCH_2SeCN$ has been investigated for the first time. The ground vibrational state spectra of the ^{80}Se and ^{78}Se isotopologues of one conformer have been assigned together with one vibrational excited-state spectrum of its ^{80}Se isotopologue. The identified rotamer has a symmetry plane (C_s symmetry) and an antiperiplanar arrangement for the C−C−Se-C chain of atoms.

The spectroscopic work has been augmented by B3LYP and MP2 quantum chemical calculations employing the 6-311++G-(3df,3pd) basis set. Both methods predict that the assigned rotamer represents the global energy minimum. The other less stable hypothetical form **sp** is predicted to have a C−C−Se−C dihedral angle of 60 (MP2) or 70.4° (B3LYP).

Comparison of the conformational properties of the title compound with the oxygen ($HC\equiv CCH_2OCN$) and sulfur ($HC\equiv CCH_2SCN$) analogues is of interest. Experimental Raman, IR, and electron diffraction data are available only for the sulfur analogue,[23] which was shown to exist as a mixture of **ap** and **sc**, with **sc** being 1.24 kJ/mol more stable than **ap** in the gaseous state at a temperature of 303 K. The present substitution of the sulfur atom with a selenium atom therefore seems to lead to the stabilization of the **ap** with respect to **sc**.

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Supporting Information Available: Microwave spectra of **ap**. This material is available free of charge via the Internet at http://pubs.acs.org.

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