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The Microwave Spectrum of Ethyl Isoselenocyanate

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The microwave spectra of two isotopic species (^{80}Se and ^{78}Se) of ethyl isoselenocyanate were measured in the frequency region of 10—28 GHz. Only a-type R-branch transitions in the ground vibrational state were identified. The rotational constants in MHz were obtained; $A=15140\pm23$, $B=1090.443\pm0.016$, and $C=1029.261\pm0.016$ for ^{80}Se species and $A=15112\pm28$, $B=1099.865\pm0.012$, and $C=1037.745\pm0.012$ for ^{78}Se species. The plausible structure of ethyl isoselenocyanate has deduced from the observed rotational constants to be the synperiplanar form with a plane of symmetry.

The microwave spectra of ethyl isocyanate[1] and ethyl isothiocyanate[2] have been reported and their structures have been determined to be planar synperiplanar conformers. A large increase in the C–N–C angle is seen when the oxygen atom of isocyanato group is replaced with a sulfur atom.[1,2] A similar trend is seen for the H–N–C angle of HNCO (124°),[3] HNCS (132°),[4] and HNCSe (143°)[5] and the C–N–C angle of CH_3NCO (140°)[6,7] and CH_3NCS (147.5°, 153°).[6,8] Recently, the C–N–C angle of methyl isoselenocyanate (CH_3NCSe)[9] has been found to be 157°. This angle is larger by about 10° than that of methyl isothiocyanate (CH_3NCS).

Franklin et al.[10] have reported the infrared spectrum of ethyl isoselenocyanate without inferring its geometrical conformation. It is very interesting to see what effect an atom heavier than oxygen or sulfur can produce on a molecular structure, particularly on the rotational conformation and the C–N–C angle.

The microwave spectra of two isotopic species (with ^{80}Se and ^{78}Se) of ethyl isoselenocyanate (CH_3CH_2NCSe) were measured in the frequency region between 10 and 28 GHz and assigned to a-type R-branch lines in the ground vibrational state. The rotational constants are reported and the molecular structure is discussed.

Experimental

Ethyl isoselenocyanate was prepared from ethyl isocyanide by refluxing in chloroform with finely divided black selenium for about 48 h.[11] Ethyl isocyanide was produced by adding silver cyanide to ethyl iodide and then adding potassium cyanide and water to the mixture.[12] Ethyl isoselenocyanate was purified by vacuum distillation and identified by comparing its infrared spectrum with the reported one.[10]

The spectrometer employed was a conventional 100 kHz square-wave Stark modulation type with a phase-sensitive detector. The microwave source was a HP8672A microwave synthesizer which was controlled by a HP9872A/S computer.

The temperature of the sample cell was kept between 0 and −10° to avoid any decomposition of the sample during the measurement of the spectrum. The absorption line widths could be kept at less than 1.5 MHz by cooling the sample cell, while the widths were about 2 to 3 MHz at room temperature.

Results and Discussion

There are four possible rotational conformers to be considered for ethyl isoselenocyanate as shown in Fig. 1. The calculation of the rotational constants for these four rotamers, using the assumed structural parameters, showed that all rotational conformers were nearly prolate symmetric top rotators, with Ray's

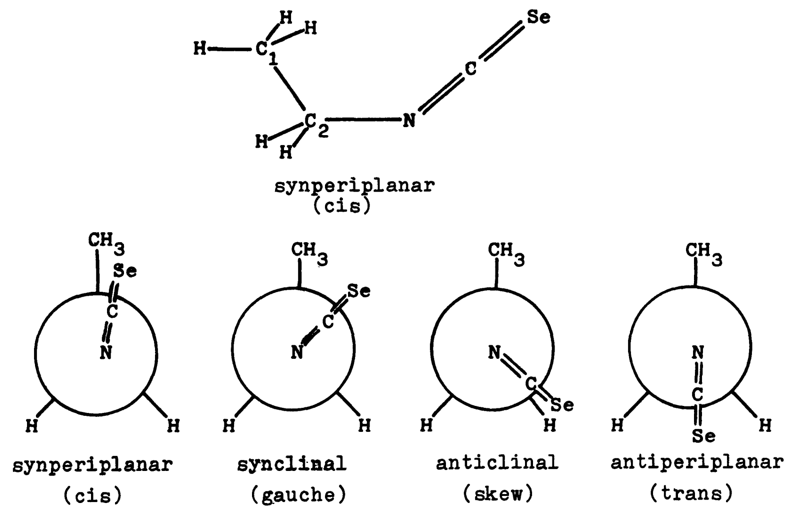

Fig. 1. Four possible rotational conformers and the numbering of carbon atoms on ethyl isoselenocyanate.

asymmetry parameter κ less than -0.99. Therefore, the rotational spectra for all four possible conformers were expected to have absorption lines with frequency intervals close to the quantity of (B+C), characteristic for a spectrum of near prolate symmetric top molecules. The ethyl isoselenocyanate has many isotopic species of selenium atom, among which ^{80}Se and ^{78}Se are dominant. The abundance ratio of ^{80}Se to ^{78}Se is about 2 and at higher frequency sides of each absorption line of ^{80}Se species, the absorption lines of ^{78}Se species were expected to appear with the intensities of about one half of the corresponding line intensities of ^{80}Se species.

The first survey of the spectrum in the frequency region of 18 to 24 GHz at the Stark field between 5 and 20 V cm^{-1} found groups of the strong lines with the frequency interval of about 2100 MHz; these were ascribed to ^{80}Se species. Groups of lines with the intensities of about one half of the corresponding line intensities of ^{80}Se species were found at frequencies higher by about 200 MHz than the absorption frequencies of ^{80}Se species. These weaker lines were assigned to ^{78}Se species.

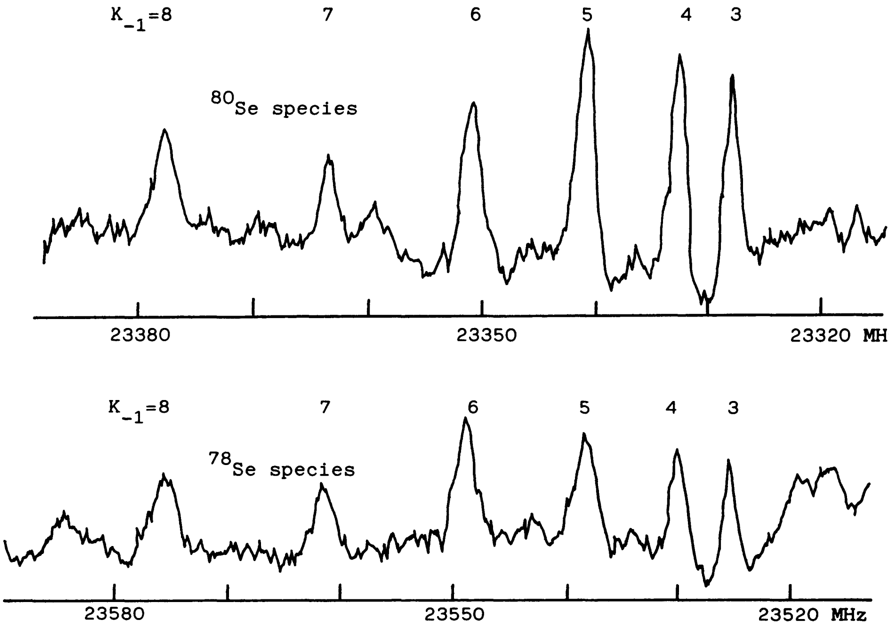

Fig. 2. The typical spectra of the J=11←10 transitions for $CH_3CH_2NC^{80}Se$ and $CH_3CH_2NC^{78}Se$, observed at the Stark field of 10 V cm^{-1}.

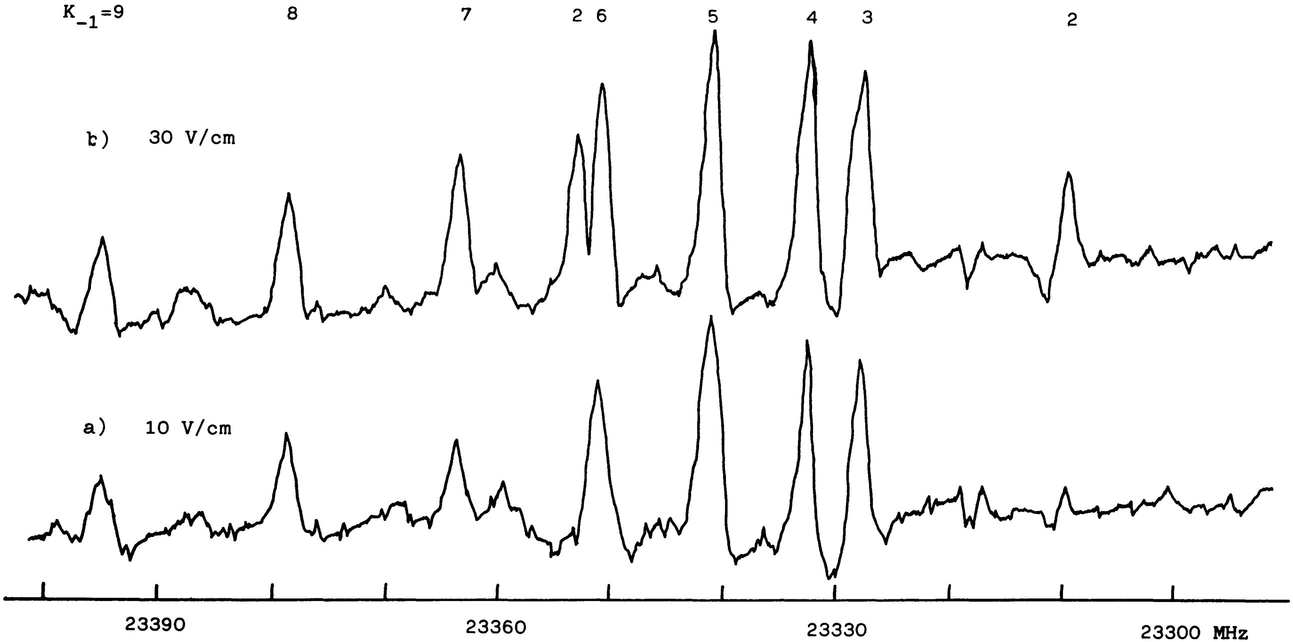

Fig. 3. The comparison of the spectra (a) and (b) for K_{-1}=2 lines. The spectra (a) and (b) were observed at the Stark fields of 10 and 30 Vcm^{-1}, respectively.

Table 1. Observed Rotational Transitions(MHz) of $CH_3CH_2NC^{80}Se$

Transition	ν_{obsd}	$\Delta\nu$ [a]	Transition	ν_{obsd}	$\Delta\nu$ [a]
$5_{15}-4_{14}$	10444.92	0.08	$10_{6}-9_{6}$	21229.05	−0.17
$5_{05}-4_{04}$	10594.25	0.10	$10_{7}-9_{7}$	21240.62	−0.20
$5_{14}-4_{13}$	10750.45	−0.21	$10_{8}-9_{8}$	21254.21	0.14
$6_{16}-5_{15}$	12533.17	0.08	$10_{9}-9_{9}$	21268.94	0.16
$6_{25}-5_{24}$	12718.95	−0.03	$10_{28}-9_{27}$	21225.55	0.01
$6_{15}-5_{14}$	12900.24	0.23	$10_{19}-9_{18}$	21492.43	0.05
$7_{17}-6_{16}$	14621.05	0.11	$11_{111}-10_{110}$	22967.22	−0.04
$7_{07}-6_{06}$	14825.79	0.06	$11_{011}-10_{010}$	23269.09	0.03
$7_{26}-6_{25}$	14838.10	0.07	$11_{210}-10_{29}$	23310.05	−0.04
$7_{3}-6_{3}$	14844.72	0.13	$11_{4}-10_{4}$	23332.72	−0.08
$7_{5}-6_{5}$	14854.09	−0.14	$11_{5}-10_{5}$	23341.13	0.12
$7_{6}-6_{6}$	14861.06	−0.16	$11_{6}-10_{6}$	23351.71	0.06
$7_{16}-6_{15}$	15048.82	−0.11	$11_{7}-10_{7}$	23364.46	0.11
$8_{18}-7_{17}$	16708.23	−0.12	$11_{8}-10_{8}$	23378.86	−0.02
$8_{08}-7_{07}$	16939.46	0.11	$11_{9}-10_{9}$	23394.87	−0.18
$8_{27}-7_{26}$	16956.63	−0.08	$11_{29}-10_{28}$	23353.74	0.07
$8_{3}-7_{3}$	16965.47	0.10	$11_{110}-10_{19}$	23638.93	0.10
$8_{4}-7_{4}$	16969.76	0.05	$12_{112}-11_{111}$	25052.19	−0.08
$8_{5}-7_{5}$	16976.16	0.10	$12_{012}-11_{011}$	25374.50	−0.09
$8_{6}-7_{6}$	16984.03	0.04	$12_{211}-11_{210}$	25426.76	−0.06
$8_{7}-7_{7}$	16993.14	−0.21	$12_{4}-11_{4}$	25453.68	−0.04
$8_{26}-7_{25}$	16973.36	−0.06	$12_{5}-11_{5}$	25462.28	−0.17
$8_{17}-7_{16}$	17197.49	0.14	$12_{9}-11_{9}$	25521.09	−0.04
$9_{19}-8_{18}$	18795.25	0.01	$12_{10}-11_{10}$	25540.50	0.14
$9_{09}-8_{08}$	19051.16	−0.09	$12_{210}-11_{29}$	25483.45	0.09
$9_{28}-8_{27}$	19074.85	−0.13	$12_{111}-11_{110}$	25784.43	−0.04
$9_{3}-8_{3}$	19086.31	0.10	$13_{113}-12_{112}$	27136.61	−0.09
$9_{4}-8_{4}$	19090.83	0.05	$13_{013}-12_{012}$	27477.64	0.05
$9_{5}-8_{5}$	19097.82	0.02	$13_{212}-12_{211}$	27542.93	−0.22
$9_{6}-8_{6}$	19106.72	0.05	$13_{4}-12_{4}$	27574.57	−0.01
$9_{7}-8_{7}$	19117.10	−0.05	$13_{5}-12_{5}$	27583.83	0.07
$9_{27}-8_{26}$	19098.66	−0.17	$13_{6}-12_{6}$	27596.23	0.16
$9_{18}-8_{17}$	19345.20	0.01	$13_{7}-12_{7}$	27610.97	0.05
$10_{110}-9_{19}$	20881.63	0.07	$13_{8}-12_{8}$	27628.13	0.14
$10_{010}-9_{09}$	21161.20	−0.02	$13_{9}-12_{9}$	27647.02	−0.01
$10_{29}-9_{28}$	21192.78	−0.01	$13_{10}-12_{10}$	27667.81	−0.02
$10_{3}-9_{3}$	21207.13	0.16	$13_{11}-12_{11}$	27690.10	−0.06
$10_{4}-9_{4}$	21211.87	0.05			

a) $\Delta\nu=\nu_{obsd}-\nu_{calcd}$.

Table 2. Observed Rotational Transitions(MHz) of $CH_3CH_2NC^{78}Se$

Transition	ν_{obsd}	$\Delta\nu$ [a]	Transition	ν_{obsd}	$\Delta\nu$ [a]
$8_{18}-7_{17}$	16847.50	0.03	$10_{5}-9_{5}$	21390.88	0.15
$8_{08}-7_{07}$	17082.05	0.08	$10_{6}-9_{6}$	21408.45	−0.10
$8_{27}-7_{26}$	17099.88	0.09	$10_{7}-9_{7}$	21420.56	−0.11
$8_{3}-7_{3}$	17108.66	0.08	$10_{28}-9_{27}$	21405.34	−0.09
$8_{4}-7_{4}$	17112.94	0.04	$10_{19}-9_{18}$	21675.93	−0.14
$8_{26}-7_{25}$	17116.96	−0.11	$11_{111}-10_{110}$	23158.04	−0.07
$8_{17}-7_{16}$	17344.46	0.13	$11_{011}-10_{010}$	23464.28	−0.08
$9_{19}-8_{18}$	18951.66	0.01	$11_{210}-10_{29}$	23506.64	−0.01
$9_{09}-8_{08}$	19211.45	−0.05	$11_{4}-10_{4}$	23529.78	0.10
$9_{28}-8_{27}$	19236.05	0.15	$11_{5}-10_{5}$	23538.05	0.08
$9_{3}-8_{3}$	19247.37	0.10	$11_{6}-10_{6}$	23548.77	−0.13
$9_{4}-8_{4}$	19252.00	0.12	$11_{7}-10_{7}$	23562.05	−0.12
$9_{5}-8_{5}$	19258.86	−0.11	$11_{29}-10_{28}$	23551.62	−0.14
$9_{6}-8_{6}$	19268.07	0.01	$12_{112}-11_{111}$	25260.46	0.19
$9_{27}-8_{26}$	19260.46	−0.11	$12_{012}-11_{011}$	25587.16	−0.11
$9_{18}-8_{17}$	19510.99*	0.39	$12_{211}-11_{210}$	25641.10	−0.05
$10_{110}-9_{19}$	21055.00	−0.21	$12_{4}-11_{4}$	25668.60	0.10
$10_{010}-9_{09}$	21339.00	−0.03	$12_{5}-11_{5}$	25677.51	0.20
$10_{29}-9_{28}$	21371.55	0.02	$12_{6}-11_{6}$	25689.01	−0.10
$10_{3}-9_{3}$	21386.23	0.17	$12_{9}-11_{9}$	25739.68	0.07
$10_{4}-9_{4}$	21390.88	0.08	$12_{210}-11_{29}$	25699.70	−0.01

a) $\Delta\nu=\nu_{obsd}-\nu_{calcd}$. *) Not included in the least-squares fitting.

The typical spectra of ^{80}Se and ^{78}Se species observed with the Stark field of 10 V cm^{-1} are shown in Fig. 2. The $K_{-1}=2$ doublet lines were observed at the Stark field of 30 V cm^{-1} as shown in Fig. 3(b). The $K_{-1}=2$ lines show a first-order Stark effect because the value (−0.991) of Ray's asymmetry parameter in ethyl isoselenocyanate is very close to −1.00. The assignments of the $K_{-1}=0$ and 1 transition lines were based on the second-order Stark effect.

In the first place, the 27 absorption lines of $J=5\leftarrow4$ to $J=13\leftarrow12$ with $K_{-1}=0$ and 1 for ^{80}Se species in the ground vibrational state were fitted to obtain the preliminary rotational and centrifugal distortion constants. These were employed to predict and assign the other transition lines with K_{-1} values larger than 2. The 75 transition lines of ^{80}Se species in the ground vibrational state were used to determine the rotational parameters, including the centrifugal distortion terms up to sextic contributions. The results are given in Tables 1, 2, and 3, together with the results of ^{78}Se species, which were obtained by analyzing the spectrum in the same way as for ^{80}Se species.

The values of −5.83 and −5.94 u Å^2 of inertia defect (Δ) for ^{80}Se and ^{78}Se species in Table 4 suggest that there are a plane symmetry and four hydrogen and heavy atoms in the ethyl isoselenocyanate molecule locate out-of-plane and in-plane, respectively. This means that there are two possible rotamers, synperiplanar and antiperiplanar forms. The observed values of P_b and Ray's asymmetry parameters for ^{80}Se and ^{78}Se species are very close to the ones calculated for synperiplanar form, but very different from the ones for antiperiplanar form, as shown in Table 4. Furthermore, the observed rotational constants A, B, and C are comparable with the ones calculated for synperiplanar conformer.

The above discussion has led to the conclusion that the spectrum assigned in this work is due to a synperiplanar rotational conformer of ethyl isoselenocyanate. This rotational conformer has been formed in ethyl isocyanate[1] and ethyl isothiocyanate.[2]

Three structural parameters, ∠C–N–C, r(C–N), and r(N=C), have been fitted to all the observed rotational constants of B and C for ^{80}Se and ^{78}Se species. The results are listed in Table 5. Other structural parameters were transferred from ethyl isocyanate,[1] ethyl isothiocyanate,[2] and carbonyl selenide.[13] The observed and calculated rotational constants obtained from the structural parameters in Table 5 are given in Table 6.

The derived values of the bond lengths, r(C–N) and r(N–C), are in agreement with those of similar compounds within less than 0.01 Å, as shown in Table 7.

Table 3. Observed Rotational(MHz) and Centrifugal Distortion(kHz) Constants for $CH_3CH_2NC^{80}Se$ and $CH_3CH_2NC^{78}Se$

	$CH_3CH_2NC^{80}Se$	$CH_3CH_2NC^{78}Se$
A	15140(23)	15112(28)
B	1090.443(16)	1099.865(12)
C	1029.261(16)	1037.745(12)
Δ_J	0.770(16)	0.793(33)
Δ_{JK}	−48.37(12)	−47.64(98)
δ_J	0.085(33)	
H_{KJ}	−0.0327(12)	
$\Delta^{a)}$	−5.83	−5.94

Values in parentheses denote 2.5 times standard deviation and apply to the last digits of the constants. Conversion factor: 505376 MHz μÅ^2. a) $\Delta=I_c-I_a-I_b$.

Table 5. Structural Parameters(Å and degree) of Synperiplanar Ethyl Isoselenocyanate

Assumed parameters	
C–H: 1.091	∠H–C–H: 108.8
C–C: 1.522	∠H_s–C–C: 109.6
C=Se: 1.709	∠C–C–H_a: 110.6
∠H=C=Se: 180	
Derived parameters	
C–N: 1.444±0.010	∠C–N–C: 158.0±3.0
N–C: 1.210±0.010	

H_s and H_a indicate the hydrogen atom located in symmetry plane and in out-of symmetry plane respectively.

Table 4. Observed and Calculated Rotational Constants(MHz), Δ (μÅ^2),$^{a)}$ and P_b(μÅ^2)$^{b)}$ of Ethyl Isoselenocyanate

	A	B	C	κ	Δ	P_b
			^{80}Se species			
Obsd	15140	1090.44	1029.26	−0.9913	−5.83	30.464
Synperiplanar	15553	1102.5	1042.9	−0.9918	−6.30	29.345
Synclinal	17491	1058.0	1013.7	−0.9946	−8.01	24.885
Anticlinal	24768	978.8	957.7	−0.9982	−9.00	15.890
Antiperiplanar	32338	945.4	929.4	−0.9990	−6.30	12.474
			^{78}Se species			
Obsd	15112	1099.87	1037.74	−0.9912	−5.94	30.476
Synperiplanar	15560	1112.1	1051.5	−0.9917	−6.30	29.335
Synclinal	17499	1067.1	1022.1	−0.9945	−8.01	24.865
Anticlinal	24775	987.2	965.7	−0.9982	−8.99	15.898
Antiperiplanar	32341	953.4	936.9	−0.9990	−6.30	12.481

a) $\Delta=I_c-I_a-I_b$. b) $P_b=(I_a+I_c-I_b)/2$.

Table 6. Observed and Calculated Rotational Constants(MHz) for $CH_3CH_2NC^{80}Se$ and $CH_3CH_2NC^{78}Se$

	$CH_3CH_2NC^{80}Se$		$CH_3CH_2NC^{78}Se$	
	Obsd	Calcd*)	Obsd	Calcd*)
A	15140	(14938)	15112	(14931)
B	1090.44	1090.31	1099.86	1099.73
C	1029.26	1029.24	1037.74	1037.66

*) Calculated using the structural parameters in Table 5.

Table 7. Comparison of Structural Parameters of R-NCX Molecules(R=H, CH_3, and C_2H_5; X=O, S, and Se)

	R-N-C/°	r(R-N)/Å	r(N=C)/Å	r(C=X)/Å
H-NCO[a]	123.9	0.995	1.214	1.1664
H-NCS[b]	131.7	0.993	1.207	1.5665
H-NCSe[c]	143.0	0.99	1.195	1.717
CH_3-NCO	139.98[d]	1.437[d]	1.207[d]	1.171[d]
	140.18[e]	1.4342[e]	1.207[e]	1.171[e]
CH_3-NCS	147.46[d]	1.452[d]	1.216[d]	1.561[d]
	152.52[f]	1.4123[f]	1.2068[f]	1.5665[f]
CH_3-NCSe[g]	157.0	1.447	1.205	1.708
C_2H_5-NCO[h]	142.11	1.461	1.207	1.171
C_2H_5-NCS[i]	151.0	1.454	1.210	1.550
C_2H_5-NCSe[j]	158.0	1.444	1.210	(1.709)

a) Ref. 3, b) Ref. 4, c) Ref. 5, d) Ref. 6, e) Ref. 7, f) Ref. 8, g) Ref. 9, h) Ref. 1, i) Ref. 2, j) Tis work, ( ): assumed.

The angle of C-N-C of 158° in ethyl isoselenocyanate is much larger than the ones of ethyl isocyanate and ethyl isothiocyanate. If the estimation error of r(C=Se) from OCSe is ±0.01 Å, the errors of r(C-N), r(N=C), and ∠C-N-C are ±0.010 Å, ±0.010 Å, and ±3°, respectively.

The R-N-C bond angle in R-NCX (R=H, CH_3, or C_2H_5 and X=O, S, or Se) molecules enlarges in order of oxygen, sulfur, and selenium atom as listed in Table 7.

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