The Microwave Spectrum and Molecular Structure of Methyl Selenocyanate

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(Received June 13, 1986)

The microwave spectra of $CH_3{}^{80}SeCN$, $CH_3{}^{78}SeCN$, $CH_3{}^{80}Se^{13}CN$, $CH_3{}^{80}SeC^{15}N$, *sym*-$CH_2D^{80}SeCN$, and *asym*-$CH_2D^{80}SeCN$ have been observed. In order to determine the rotational constants of $^{13}CH_3{}^{80}SeCN$, we used the transition frequencies observed by Landsberg. From these spectra the complete r_s coordinates of seven atoms have been calculated using Kraitchman's equation. The structural parameters (bond lengths in Å(1Å=0.1 nm) and angles in degree) are: r(C1-H1)=1.073(4), r(C1-H2)=1.083(6), r(C1-Se)=1.954(7), r(Se-C2)=1.836(11), r(C2-N)=1.162(9), ∠H1-C1-H2=110.6(6), ∠H2-C1-H2′=111.4(3), ∠H1-C1-Se=105.4(5), ∠H2-C1-Se=109.3(6), ∠C1-Se-C2=96.0(11), and ∠Se-C2-N=179.3(15). It was found from the r_s structural parameters that the methyl group is at a staggered position with respect to the cyano group, the methyl group does not show C_{3v} symmetry, the bond length of r(Se-C2) is much shorter than that of r(Se-C1), and the chain bond of Se-C2-N is linear.

In a previous paper,[1] we reported on the microwave spectra, the rotational constants, the dipole moments, the barrier heights of the methyl internal rotation, the first excited state of the methyl torsional mode, and the r_o structure of methyl selenocyanate (with ^{80}Se, ^{78}Se, ^{77}Se, and ^{76}Se) and methyl selenocyanate-d_3 (with ^{80}Se and ^{78}Se).

The selenocyanates are interesting molecules for several reasons. When a selenium atom is bonded to a cyano group, it is expected that the bond length of r(Se-C2) will be shorter than the normal single-bond length. The numbering of the atoms on the methyl selenocyanate is shown in Fig. 1. Another question is whether the chain bond of Se-C2-N is linear or bent.

In this research four isotopic species were newly prepared and the spectra were observed. The r_s structural parameters of methyl selenocyanate were calculated from the r_s coordinates of all atoms. The r_s structural parameters obtained are compared with those of related molecules and are discussed.

Experimental

The sample of methyl selenocyanate-*d* (CH_2DSeCN) was prepared by a reaction of methyl-*d* iodide (99% D, Merck Sharp & Dohme Canada) with potassium selenocyanate according to the method used for normal species.[1] The isotopic species of $CH_3Se^{13}CN$ and $CH_3SeC^{15}N$ were prepared by mixing potassium selenocyanate-^{13}C or potassium selenocyanate-^{15}N with methyl iodide. The potassium selenocyanate-^{13}C and potassium selenocyanate-^{15}N were synthesized by mixing potassium cyanide-^{13}C (91.6% ^{13}C, British Oxygen Co. Ltd.) or potassium cyanide-^{15}N (96.6% ^{15}N, Boxy Brown Co. Ltd.) with black selenium in ethanol.

The spectra were observed in the frequency region from 8.0 to 37 GHz with a conventional 100-kHz Stark modulation microwave spectrometer. The microwave source employed was a synthesized signal generator (HP 8672A). The absorption cell was cooled to about −20 °C with dry ice.

Results and Discussion

In order to determine as accurately as possible the rotational constants which are used to calculate the r_s coordinates of the Se atom, several a-type R-branch transitions of ^{80}Se and ^{78}Se species for which the discrepancies between the observed and the calculated frequencies were large in the previous measurement[1] were remeasured. In addition, a-type Q-branch transitions were newly assigned as listed in Table 1. The microwave spectra of $CH_3{}^{80}Se^{13}CN$ and $CH_3{}^{80}SeC^{15}N$ were newly observed and were assigned as listed in Table 2. In partially deuterated methyl selenocyanate, two conformations are possible. The symmetrical conformer (sym-species) has a plane of symmetry whereas the asymmetrical conformer (asym-species) exists in two equivalent forms. The sym-species shows the spectrum of an ordinary asymmetric rigid-rotor while the asym-species is expected to show splittings due to a tunnelling effect through the two equivalent potential wells. The observed transitions of *sym*-$CH_2D^{80}SeCN$ were assigned as listed in Table 3. The a-type R-branch transitions in asym-species were little affect by the tunnelling effect, but small splittings due to the tunnelling effect in a-type Q-branch transitions were observed. The center frequencies of the splittings observed in the Q-branch transitions were used to fit the rigid-rotor approximation Hamiltonian. The observed transitions of *asym*-$CH_2D^{80}SeCN$ were assigned as shown in Table 4. The rotational and cen-

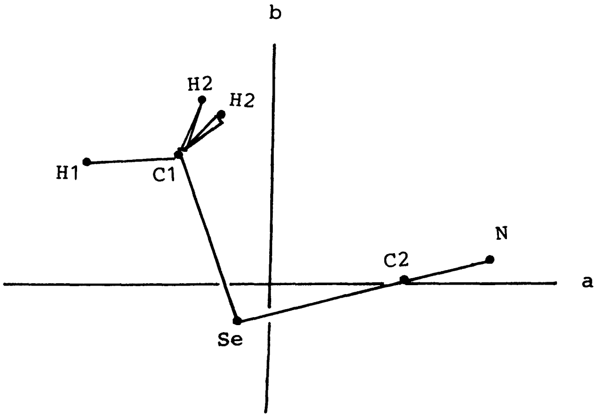

Fig. 1. The numbering of the atoms on methyl selenocyanate.

Table 1. Observed Transition Frequencies (MHz) of CH_3SeCN in the Ground State (A-species)

Transition	$^{12}CH_3{}^{80}Se^{12}C^{14}N$		$^{12}CH_3{}^{78}Se^{12}C^{14}N$		Transition	$^{12}CH_3{}^{80}Se^{12}C^{14}N$		$^{12}CH_3{}^{78}Se^{12}C^{14}N$	
	ν_{obsd}	$\Delta\nu^{a)}$	ν_{obsd}	$\Delta\nu^{a)}$		ν_{obsd}	$\Delta\nu^{a)}$	ν_{obsd}	$\Delta\nu^{a)}$
$3_{13}-2_{12}$	17021.77	(−0.05)*b)	17074.96	(−0.02)*b)	$8_{26}-8_{27}$	11711.77	(−0.01)		
$3_{03}-2_{02}$	18043.38	(0.03)*	18098.33	(−0.07)*	$9_{27}-9_{28}$	16526.87	(0.12)	16482.10	(−0.02)
$3_{22}-2_{21}$	18345.52	(0.11)*	18398.46	(−0.15)*	$10_{28}-10_{29}$	22086.54	(−0.03)	22039.30	(0.06)
$3_{21}-2_{20}$			18699.52	(0.21)*	$11_{29}-11_{210}$	28250.88	(−0.03)	28206.13	(−0.04)
$3_{12}-2_{11}$	19573.39	(−0.03)*	19627.14	(−0.05)*	$13_{310}-13_{311}$	18936.08	(−0.03)	18822.12	(0.05)
$4_{14}-3_{13}$	22615.80	(−0.07)	22687.21	(−0.02)*	$14_{311}-14_{312}$	25076.00	(−0.02)	24949.55	(−0.04)
$4_{04}-3_{03}$	23729.26	(−0.18)*	23804.26	(−0.07)*	$17_{413}-17_{414}$	20262.50	(−0.03)	20066.45	(−0.01)
$4_{23}-3_{22}$	24400.93	(0.13)*	24472.08	(−0.07)*	$18_{414}-18_{415}$	26854.15	(−0.01)	26631.80	(0.07)
$4_{22}-3_{21}$	25132.05	(−0.03)*	25199.60	(0.09)*	$21_{516}-21_{517}$	20746.94	(−0.03)	20463.20	(−0.14)
$4_{13}-3_{12}$	25997.93	(0.07)*	26070.38	(0.11)*	$22_{517}-22_{518}$	27650.34	(0.21)	27321.62	(0.03)
$5_{15}-4_{14}$	28152.88	(−0.29)*	28242.88	(−0.13)*	$25_{619}-25_{620}$	20576.30	(−0.06)	20206.15	(0.02)
$5_{05}-4_{04}$	29201.02	(−0.02)*	29296.38	(0.02)*	$26_{620}-26_{621}$	27646.12	(−0.16)	27208.15	(−0.12)
$5_{24}-4_{23}$	30405.52	(0.09)	30495.37	(0.09)	$29_{722}-29_{723}$	19907.97	(0.01)	19457.71	(0.08)
$5_{23}-4_{22}$	31778.89	(0.09)	31862.22	(0.02)	$30_{723}-30_{724}$	27002.00	(0.07)	26457.68	(0.11)
$5_{14}-4_{13}$	32323.58	(0.15)	32415.27	(0.02)	$33_{825}-33_{826}$	18877.46	(0.01)	18357.90	(−0.06)
$6_{15}-6_{16}$	17537.79	(0.04)	17545.78	(0.02)	$34_{826}-34_{827}$	25861.47	(−0.01)	25219.78	(0.01)
$7_{16}-7_{17}$	22993.91	(0.01)	23008.85	(0.01)	$38_{929}-38_{930}$	24356.49	(0.01)	23631.50	(0.01)
$8_{17}-8_{18}$	28850.67	(−0.12)	28877.08	(−0.06)					

a) $\Delta\nu = \nu_{obsd} - \nu_{calcd}$. b) The values marked by * are the remeasured ones for the reported values of the previous paper.[1)]

Table 2. Observed Transition Frequencies (MHz) of $CH_3{}^{80}Se^{13}CN$ and $CH_3{}^{80}SeC^{15}N$ in the Ground State (A-species)

Transition	$CH_3{}^{80}Se^{13}CN$		$CH_3{}^{80}SeC^{15}N$		Transition	$CH_3{}^{80}Se^{13}CN$		$CH_3{}^{80}SeC^{15}N$	
	ν_{obsd}	$\Delta\nu^{a)}$	ν_{obsd}	$\Delta\nu^{a)}$		ν_{obsd}	$\Delta\nu^{a)}$	ν_{obsd}	$\Delta\nu^{a)}$
$2_{12}-1_{11}$	11260.61	(0.04)	10989.63	(0.06)	$9_{27}-9_{28}$	15967.17	(0.02)	14780.68	(0.09)
$2_{02}-1_{01}$	12021.23	(0.06)	11717.44	(−0.20)	$10_{28}-10_{29}$	21389.96	(0.09)	19901.72	(0.00)
$2_{11}-1_{10}$	12927.67	(−0.03)	12576.74	(−0.23)	$13_{310}-13_{311}$	18033.19	(−0.13)	16156.28	(−0.02)
$3_{13}-2_{12}$	16846.78	(−0.27)	16444.93	(0.07)	$14_{311}-14_{312}$	23981.66	(0.07)	21681.78	(−0.02)
$3_{02}-2_{02}$	17852.76	(−0.07)	17415.17	(0.03)	$17_{413}-17_{414}$	18992.20	(0.03)	16405.62	(−0.01)
$3_{22}-2_{21}$	18140.80	(−0.12)	17674.87	(0.22)	$18_{414}-18_{415}$	25322.60	(−0.04)	22159.96	(0.01)
$3_{21}-2_{20}$	18429.12	(−0.20)	17934.16	(−0.28)	$21_{516}-21_{517}$	19110.62	(−0.08)	15857.74	(−0.07)
$3_{12}-2_{11}$	19343.78	(0.09)	18822.51	(0.01)	$22_{517}-22_{518}$	25667.60	(0.01)	21655.04	(0.04)
$4_{14}-3_{13}$	22386.30	(−0.07)	21857.31	(−0.05)	$25_{619}-25_{620}$	18599.74	(−0.10)	14776.77	(0.01)
$4_{04}-3_{03}$	23489.63	(0.08)	22935.11	(0.00)	$26_{620}-26_{621}$	25224.85	(0.02)	20438.29	(−0.01)
$4_{23}-3_{22}$	24130.80	(−0.16)	23515.00	(0.01)	$29_{722}-29_{723}$	17637.16	(−0.05)	13378.07	(0.09)
$4_{32}-3_{31}$			23687.55	(0.20)	$30_{723}-30_{724}$	24178.56	(−0.05)	18748.78	(−0.05)
$4_{31}-3_{30}$			23707.71	(−0.01)	$31_{724}-31_{725}$			25338.89	(−0.01)
$4_{22}-3_{21}$	24829.25	(0.20)	24146.15	(−0.07)	$33_{825}-33_{826}$	16372.79	(−0.01)	11831.73	(−0.07)
$4_{13}-3_{12}$	25696.72	(0.20)	25011.74	(0.07)	$34_{826}-34_{827}$	22695.23	(0.11)	16792.44	(−0.04)
$5_{14}-5_{15}$	12391.85	(−0.15)	11810.81	(0.12)	$35_{827}-35_{828}$			23034.66	(0.06)
$6_{15}-6_{16}$	17175.81	(0.00)	16387.40	(0.05)	$38_{929}-38_{930}$	20922.30	(−0.07)	14737.60	(0.04)
$7_{16}-7_{17}$	22537.70	(−0.01)	21538.16	(−0.12)	$39_{930}-39_{931}$			20503.87	(−0.03)
$8_{26}-8_{27}$	11286.95	(−0.02)	10392.68	(0.14)					

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

trifugal distortion constants obtained for normal and isotopic species are listed in Table 5 except for $^{13}CH_3{}^{80}SeCN$ species.

For the $^{13}CH_3{}^{80}SeCN$ species, Landsberg[2)] has determined the rotational constants by using the frequencies of the a-type R-branch transition, but has not determined the centrifugal distortion constants. We obtained the rotational constants by using a Hamiltonian which included the centrifugal distortion effects for all of isotopic species. Therefore, in order to consider the effects for $^{13}CH_3{}^{80}SeCN$ species, we used the centrifugal distortion constants of $CH_3{}^{80}SeCN$ as those of $^{13}CH_3{}^{80}SeCN$. The rotational constants of $^{13}CH_3{}^{80}SeCN$ were calculated by using the assumed centrifugal distortion constants and the frequencies of an a-type R-branch transition observed by Landsberg.[2)] The obtained rotational constants are listed in Table 5 and are in good agreement with those reported by Landsberg.[2)]

The obtained values of moments of inertia and the planar moments of inertia,[3)] P_c, are shown in Table 6. The values of P_c in isotopic species were close to 1.42

Table 3. Observed Transition Frequencies (MHz) of *sym*-$CH_2D^{80}SeCN$ in the Ground State

Transition	ν_{obsd}	$\Delta\nu$[a]	Transition	ν_{obsd}	$\Delta\nu$[a]	Transition	ν_{obsd}	$\Delta\nu$[a]
$2_{12}-1_{11}$	11005.00	(−0.28)	$6_{15}-6_{16}$	17047.59	(0.01)	$24_{6,18}-24_{6,19}$	14788.34	(0.04)
$2_{02}-1_{01}$	11758.20	(−0.33)	$7_{16}-7_{17}$	22343.51	(−0.07)	$25_{6,19}-25_{6,20}$	20625.76	(0.11)
$3_{13}-2_{12}$	16462.98	(0.18)	$8_{17}-8_{18}$	28021.84	(0.11)	$26_{6,20}-26_{6,21}$	27607.25	(−0.01)
$3_{03}-2_{02}$	17453.68	(0.15)	$9_{27}-9_{28}$	16152.60	(−0.10)	$28_{7,21}-28_{7,22}$	14310.83	(0.03)
$3_{12}-2_{11}$	18943.91	(−0.14)	$10_{28}-10_{29}$	21565.26	(−0.05)	$29_{7,22}-29_{7,23}$	20099.78	(0.03)
$4_{14}-3_{13}$	21871.89	(−0.07)	$12_{2,10}-12_{2,11}$	33948.86	(−0.05)	$30_{7,23}-30_{7,24}$	27143.31	(0.03)
$4_{04}-3_{03}$	22949.30	(0.11)	$13_{3,10}-13_{3,11}$	18612.76	(0.07)	$32_{8,24}-32_{8,25}$	13568.10	(0.15)
$4_{23}-3_{22}$	23608.57	(−0.03)	$14_{3,11}-14_{3,12}$	24605.00	(−0.11)	$33_{8,25}-33_{8,26}$	19199.69	(−0.17)
$4_{13}-3_{12}$	25160.26	(−0.02)	$16_{4,12}-16_{4,13}$	14489.29	(−0.02)	$35_{8,27}-35_{8,28}$	34430.50	(−0.06)
$5_{15}-4_{14}$	27225.50	(−0.03)	$17_{4,13}-17_{4,14}$	20038.88	(−0.03)	$36_{9,27}-36_{9,28}$	12649.24	(−0.14)
$5_{05}-4_{04}$	28235.50	(−0.03)	$18_{4,14}-18_{4,15}$	26492.68	(0.15)	$37_{9,28}-37_{9,29}$	18034.30	(−0.15)
$5_{24}-4_{23}$	29416.69	(−0.11)	$20_{5,15}-20_{5,16}$	14891.50	(−0.18)	$38_{9,29}-38_{9,30}$	24827.43	(0.21)
$5_{23}-4_{22}$	30764.08	(0.17)	$21_{5,16}-21_{5,17}$	20653.00	(−0.10)	$39_{9,30}-39_{9,31}$	33013.00	(−0.06)
$5_{14}-4_{13}$	31279.39	(0.31)	$22_{5,17}-22_{5,18}$	27438.29	(0.12)	$40_{10,30}-40_{10,31}$	11627.79	(0.10)

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

Table 4. Observed Transition Frequencies (MHz) of *asym*-$CH_2D^{80}SeCN$ in the Ground State

Transition	ν_{obsd}	$\Delta\nu$[a]	Transition	ν_{obsd}	$\Delta\nu$[a]	Transition	ν_{obsd}	$\Delta\nu$[a]
$2_{12}-1_{11}$	11165.00	(0.20)	$6_{15}-6_{16}$	18014.23	(0.17)	$22_{5,17}-22_{5,18}$	12091.18 12092.56	(0.06)
$2_{02}-1_{01}$	11953.15	(−0.38)	$7_{16}-7_{17}$	23484.53	(−0.08)	$23_{6,17}-23_{6,18}$	17532.66 17534.57	(−0.01)
$2_{11}-1_{10}$	12927.64	(−0.04)	$8_{17}-7_{18}$	29244.22	(−0.15)	$24_{6,18}-24_{6,19}$	24214.34 24216.50	(0.12)
$3_{13}-2_{12}$	16691.86	(−0.08)	$8_{26}-8_{27}$	13182.00	(0.24)	$25_{6,19}-25_{6,20}$	31994.38 31997.08	(0.06)
$3_{03}-2_{02}$	17705.08	(0.11)	$9_{27}-9_{28}$	18318.50	(0.06)	$26_{6,20}-26_{6,21}$	13048.50 13050.00	(−0.03)
$3_{12}-2_{11}$	19330.00	(−0.07)	$10_{28}-10_{29}$	24120.00	(0.01)	$27_{7,20}-27_{7,21}$	18800.68 18802.89	(−0.15)
$4_{14}-3_{13}$	22160.88	(−0.08)	$11_{29}-11_{2,10}$	30392.45	(−0.02)	$30_{7,23}-30_{7,24}$	13797.30 13799.67	(−0.19)
$4_{04}-3_{03}$	23220.79	(−0.08)	$12_{2,10}-12_{2,11}$	36902.49 36903.44	(0.12)	$31_{8,23}-31_{8,24}$	19801.35 19803.36	(0.10)
$4_{23}-3_{22}$	24019.66	(0.02)	$14_{3,11}-14_{3,12}$	29251.00 29252.00	(−0.15)	$32_{8,24}-32_{8,25}$	27223.00 27225.62	(−0.16)
$4_{22}-3_{21}$	24891.00	(0.14)	$15_{4,11}-15_{4,12}$	14038.43 14039.63	(−0.02)	$34_{8,26}-34_{8,27}$	14363.84 14365.56	(−0.04)
$4_{13}-3_{12}$	25650.04	(0.03)	$16_{4,12}-16_{4,13}$	19710.51 19711.53	(0.17)	$35_{8,27}-35_{8,28}$	20563.34 20565.49	(−0.01)
$5_{15}-4_{14}$	27564.82	(−0.04)	$18_{4,14}-18_{4,15}$	33640.85 33643.25	(0.12)	$36_{9,27}-36_{9,28}$	28265.28 28268.36	(0.21)
$5_{05}-4_{04}$	28506.50	(0.06)	$19_{5,14}-19_{5,15}$	15960.50 15962.00	(−0.03)	$38_{10,28}-38_{10,29}$	14767.75 14769.83	(−0.02)
$5_{24}-4_{23}$	29908.83	(−0.05)	$20_{5,15}-20_{5,16}$	22173.62 22175.45	(0.03)	$39_{10,29}-39_{10,30}$	21113.15 21115.76	(0.29)
$5_{23}-4_{22}$	31514.75	(−0.08)	$21_{5,16}-21_{5,17}$	29395.40 29397.50	(−0.07)	$40_{10,30}-40_{10,31}$	29038.47 29041.62	(−0.25)
$5_{14}-4_{13}$	31845.75	(0.02)						

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

uÅ^2 (1 uÅ^2=1.66053×10^{-29} kg(nm)^2) except for *asym*-CH_2DSeCN. This is in conformity with the fact that the heavy atoms (C1, Se, C2, and N) and the deuterium atom in the methyl group are located in the symmetry plane. The large value (2.159 uÅ^2) of P_c of *asym*-CH_2DSeCN agrees with the fact that the deuterium atom of the methyl group is located out of the plane.

The coordinates of the atoms in the principal-axis system of the normal species ($CH_3{}^{80}SeCN$), as obtained using Kraitchman's equation,[4] are listed in Table 7. The b-coordinate of C2 atom obtained from Kraitchman's equation was small (0.0898 Å) and unreliable. Therefore, the b-coordinate of C2 was calculated from the first moment equation. Although the c-coordinates(Å) of H1, C1, Se, C2, and N obtained from Kraitchman's equation were found to be either extremely small or imaginary (0.1557(121), 0.0032*i*, 0.0002*i*, 0.0272(674), and 0.0019*i*), respectively, these c-

Table 5. Observed Rotational (MHz) and Centrifugal Distortion (kHz) Constants in A-Species[a]

Species	A	B	C	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
$CH_3{}^{80}SeCN$	10143.93(35)	3483.665(33)	2631.619(33)	0.80(78)	14.7(23)	14.6(25)	0.425(73)	10.0(33)
$CH_3{}^{78}SeCN$	10198.33(20)	3492.634(90)	2640.404(83)	0.8[b]	14.1(8)	14.6[b]	0.444(13)	8.8(13)
$^{13}CH_3{}^{80}SeCN$[c]	9725.60(60)	3454.943(20)	2586.432(18)	0.8[b]	14.7[b]	14.6[b]	0.425[b]	10.0[b]
$CH_3{}^{80}Se^{13}CN$	10142.18(23)	3440.361(13)	2606.736(12)	0.8[b]	14.5(10)	14.6[b]	0.403(15)	10.2(15)
$CH_3{}^{80}SeC^{15}N$	10122.20(21)	3342.726(13)	2548.964(12)	0.8[b]	14.2(10)	14.6[b]	0.366(11)	9.6(11)
a-$CH_2D^{80}SeCN$	9270.81(7)	3452.336(38)	2570.825(38)	1.4(9)	13.1(2)	14.6[b]	0.436(53)	10.0[b]
s-$CH_2D^{80}SeCN$	9775.95(14)	3372.768(13)	2544.179(12)	0.8[b]	10.5(7)	14.6[b]	0.490(5)	6.1(9)

a) The values of A-species for the molecules except for mono-dueterated species are given. Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviation. b) The assumed values of the centrifugal distortion constants in normal species were used. c) The transition frequencies observed by Landsberg[2] were used.

Table 6. Observed Moments of Inertia[a] (uÅ²) and P_c (uÅ²)

Species	I_a	I_b	I_c	P_c
$CH_3{}^{80}SeCN$	49.8205(17)	145.0702(14)	192.0400(24)	1.4254(28)
$CH_3{}^{78}SeCN$	49.5548(10)	144.6977(37)	191.4010(60)	1.4258(54)
$^{13}CH_3{}^{80}SeCN$	51.9633(32)	146.2762(8)	195.3950(14)	1.4223(27)
$CH_3{}^{80}Se^{13}CN$	49.8291(11)	146.8962(6)	193.8731(9)	1.4261(13)
$CH_3{}^{80}SeC^{15}N$	49.9275(10)	151.1867(6)	198.2672(9)	1.4235(13)
a-$CH_2D^{80}SeCN$	54.5126(4)	146.3867(16)	196.5813(29)	2.1590(25)
s-$CH_2D^{80}SeCN$	51.6958(7)	149.8401(6)	198.6401(9)	1.4479(11)

a) Conversion factor is 505376 uÅ²MHz. Figures in parentheses indicate the uncertainty attached to the last significant figures estimated from 2.5 times the standard deviations. (1 uÅ² = 1.66053×10^{-29} kg(nm)²). b) $P_c=(I_a+I_b-I_c)/2$.

Table 7. r_s Coordinates of Atoms[a] (in Å) (1 Å=0.1 nm)

Atom	*a*	*b*	*c*
H1	−2.1596(8)	1.3958(13)	0.0[b]
H2	−0.7462(30)	1.9820(12)	0.8946(29)
H2′	−0.7462(30)	1.9820(12)	−0.8946(29)
C1(methyl)	−1.0898(27)	1.4779(20)	0.0[b]
Se	−0.4289(29)	−0.3611(34)	0.0[b]
C2(cyanide)	1.3543(13)	0.0775(237)[c]	0.0[b]
N	2.4860(7)	0.3422(57)	0.0[b]

a) The numbering of the atoms is shown in Fig. 1. Atomic masses taken from W. Gordy and R. L. Cook, Microwave Molecular Spectra, third ed. (John Wiley & Sons, Inc., New York, 1984) Appendix E. b) Assumed to be zero by symmetry. c) Obtained by first-moment relation, $\sum m_i b_i=0$.

Table 8. r_s Structure[a] of Methyl Selenocyanate

r(C1–H1) :	1.073(4)	∠H1–C1–H2 :	110.6(6)
r(C1–H2) :	1.083(6)	∠H2–C1–H2′ :	111.4(3)
r(C1–Se) :	1.954(7)	∠H1–C1–Se :	105.4(5)
r(Se–C2) :	1.836(11)	∠H2–C1–Se :	109.3(6)
r(C2–N) :	1.162(9)	∠C1–Se–C2 :	96.0(11)
		∠Se–C2–N :	179.3(15)

a) Bond lengths are in Å (1 Å=0.1 nm) and angles are in degree.

coordinates are assumed to be zero because the heavy atoms and H1 atom is located in the symmetry plane. The structural parameters obtained are listed in Table 8.

Table 9. Comparison of r_s Structural Parameters of Methyl Group in CH_3SeCN and CH_3SCN (Bond Lengths in Å and Angles in degree)

	CH_3SeCN[a]	CH_3SCN[b]
r(C1–H1)	1.073(4)	1.073(3)
r(C1–H2)	1.083(6)	1.086(4)
∠H1–C1–H2	110.6(6)	110.3(2)
∠H2–C1–H2′	111.4(3)	111.3(2)
∠H1–C1–M[c]	105.4(5)	105.4(3)
∠H2–C1–M[c]	109.3(6)	109.7(1)

a) This work. b) Ref. 5. c) M=Se or S atom.

The r_s structural parameters of the methyl group for CH_3SeCN were compared with those for CH_3SCN[5] as listed in Table 9. The structural parameters of the methyl group for CH_3SeCN are quite similar to those for CH_3SCN. The bond length of *r*(C1–H1) for CH_3SCN has been found to be shorter by about 0.01 Å than that of *r*(C1–H2).[5] The numbering of the atoms of CH_3SCN is the same as that of CH_3SeCN, as shown in Fig. 1. Although a similar trend can be seen for CH_3SeCN, the bond length of *r*(C1–H1) agrees with that of *r*(C1–H2) within the limits of error. The two H–C–H angles are almost the same, but the angle of H1–C1–Se is much smaller than that of H2–C1–Se. Neither the methyl group of CH_3SeCN nor that of CH_3SCN shows a C_{3v} symmetry. The methyl group is staggered with respect to the cyano group.

The r_s structural parameters of CH_3SeCN were compared with those of related molecules as listed in Table

Table 10. Comparison of the Structural Parameters of CH_3SeCN with Those of Related Molecules. (Bond Lengths in Å and Angles in degree).

	r(C1-Se)	∠C1-Se-C2	r(Se-C2)	r(C2≡N)	∠Se-C2≡N
CH_3SeCH_3[a] (r_s)	1.943(1)	96.2(2)	1.943(1)		
CH_3SeCN[b] (r_s)	1.954(7)	96.0(11)	1.836(11)	1.162(9)	179.3(15)
$CH_3C(H)$=Se[c] (r_0)			1.758(10)		
CH_3CN[d] (r_s)				1.157(1)	
CH_3SCN[e] (r_s)	1.824(2)[f]	99.03(8)[g]	1.684(3)[h]	1.170(2)	179.8(13)[i]

a) Ref. 6. b) This work. c) Ref. 7. d) Ref. 8. e) Ref. 5. f) r(C1-S). g) ∠C1-S-C2. h) r(S-C2). i) ∠S-C2≡N.

10. The bond length of r(C1-Se) is almost the same as that for a normal single bond of CH_3SeCH_3.[6] On the other hand, the bond length of r(Se-C2) comes between those of a single bond and a double bond and has the value which is shorter by about 0.1 Å than a normal single bond[6] and is longer by about 0.1 Å than a normal double bond of $CH_3C(H)$=Se.[7] This intermediate bond length arises from the back donation of electrons from the selenium atom to a cyano group. The same trend has also been seen in the bond length of r(C1-S) and r(S-C2) of methyl thiocyanate,[5] as shown in Table 10. The bond length of r(C2-N) of methyl selenocyanate agrees with that of CH_3CN[8] within 0.01 Å. The bond angle of C1-Se-C2 is similar to that of CH_3SeCH_3[6] but is smaller by about 3° than that of C1-S-C2 of methyl thiocyanate.[5] Both the chain bonds of Se-C2-N of methyl selenocyanate and that of S-C2-N of methyl thiocyanate[5] were found to be linear.

It was concluded from the r_s structural parameters of methyl selenocyanate that (i) the methyl group is staggered with respect to the cyano group, (ii) the bond angle of H1-C1-Se is much smaller than that of H2-C1-Se and the methyl group does not have the C_{3v} symmetry, (iii) the bond length of r(Se-C(N)) is much shorter than that of r(Se-C(CH_3)) because of the back donation of electrons in bonding a selenium atom to a cyano group, and (iv) the chain bond of Se-C2-N is linear.

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