The Microwave Spectrum of Methyl Isoselenocyanate

Takeshi SAKAIZUMI,* Atsushi YASUKAWA, Hirobumi MIYAMOTO, Osamu OHASHI, and Ichiro YAMAGUCHI
Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102
(Received December 9, 1985)

Synopsis. The microwave rotational spectra of two isotopic species of methyl isoselenocyanate(CH_3NCSe with ^{80}Se and ^{78}Se) in the ground vibrational state(A-species) have been assigned in the 9 to 40 GHz frequency range and the rotational and centrifugal distortion constants for the ground vibrational state have been determined. Three r_0 structural parameters have been determined from the observed rotational constants of the two species.

Molecules with an isoselenocyanato group form rather intriguring compounds since the isoselenocyanato(NCSe) group is ambidexterous: the isoselenocyanato group is able to bond at the site of either the N or the Se atom, forming either a R-NCSe or a R-SeCN molecule. The isoselenocyanic acid(H-NCSe)[1] exists only as R-NCSe type in the gas phase, while methyl derivatives have been identified as CH_3-SeCN[2] and CH_3-NCSe.[3] The presence of methyl isoselenocyanate(CH_3-NCSe) has been detected by infrared spectroscopy.[3]

In the CH_3-NCX(X=O and S) type, a barrier to the internal rotation of the methyl group in CH_3NCO[4] and CH_3NCS[4] has been found to be 83 and 304 cal mol^{-1} from the splitting of the $K_{-1}=0$, $m=\pm3$ lines. On the other hand, in the CH_3-XCN(X=S and Se) type, the barrier to internal rotation in CH_3SCN[5] and CH_3SeCN[2] has been found to be 1600 and 1240 cal mol^{-1}.

We are interested in the bond angle for R-NCX (R=H, CH_3, C_2H_5 and X=O, S, Se) molecules. The angle of H-N-C for H-NCO,[6] H-NCS,[7] and H-NCSe[1] has been determined to be 123.9°, 131.7°, and 143°. In methyl derivatives, the angle of C-N-C of CH_3-NCO[4] and CH_3-NCS[4] has been determined to be 139.98° and 147.5°. Recently, the C-N-C equilibrium angle for CH_3NCO[8] and CH_3NCS[9] has been found to be 140.2° and 152.5°, using a quasi-symmetric top molecule approach. These data show a large increase of 7 to 12° in the R-N-C angle for R-NCX molecules when the oxygen atoms of R-NCO molecules are replaced by sulfur atoms. A further increase in the C-N-C angle is anticipated upon the replacement of the sulfur atom in CH_3NCS by a selenium atom.

In this paper the microwave spectrum and three structural parameters of methyl isoselenocyanate in the ground vibrational state are reported.

Experimental

Methyl isoselenocyanate was prepared by heating in chloroform a mixture of methyl isocyanide, which was synthesized according to the method of Schuster,[10] and selenium powder for 96 hours.[3] The sample was purified by trap-to-trap vacuum distillation. The melting point and the IR spectrum agreed with the literature.[3]

The rotational spectrum was observed in the frequency region from 9 to 40 GHz with a conventional 100-kHz square-wave Stark modulation spectrometer. The microwave sources employed were a singnal generator(HP-8672A) in the frequency region of 9 to 23 GHz and a YIG-tuned GaAs oscillator(WJ-5610-302FD) in the frequency region of 26.5 to 40 GHz. The wave-guide cell was cooled with dry ice to about 0—10 °C.

Results and Discussion

The observed spectrum was quite dense, presumably due to the presence of several isotopic species (^{82}Se, ^{80}Se, ^{78}Se, and ^{76}Se), their vibrationally-excited states, and the A-E splitting due to the internal rotation of the methyl group.

A typical spectrum showed a-type R-branch transitions with the characteristic K-structure. The assignment of each line for the ^{80}Se species was made on the basis of the Stark effect, the relative population of the ^{80}Se species, and the fact that the line intensity for a ground state is the strongest. The assignment of the spectrum for the ^{78}Se species was made according to the estimated isotopic shifts of lines, keeping in mind that the spectrum lines have the same Stark effect as the corresponding lines of the ^{80}Se species. The observed and calculated line frequencies of ^{80}Se and ^{78}Se species are in good agreement, as shown in Tables 1 and 2. The rotational and centrifugal distortion constants were obtained by the least-squares method; they are listed in Table 3. The transitions listed in Tables 1 and 2 are ascribed to the A-species in the ground vibrational state for ^{80}Se and ^{78}Se species because of their Stark effects and line intensities. Since no Q-branch lines were observed because of their low intensity, the rotational constants A could not be determined accurately.

The observed spectra of CH_3NCO[4] and CH_3NCS[4] could not be fitted by the usual semirigid internal-rotation treatment. A reasonable fit of the $K_{-1}=0$ lines was obtained only if a semiempirical nonrigid correction factor[4] was used. The observed spectrum of CH_3NCSe could be fitted by the rigid-rotor approximation. This may mean that the barrier to internal rotation of the methyl group in CH_3NCSe may be higher than that in CH_3NCS(304 cal mol^{-1}). The E-species lines could not be assigned because the observed spectrum was quite dense.

Three structural parameters, r(C-N), r(N=C), and ∠C-N-C, have been adjusted to make the calculated values fit the four observed rotational constants of B and C. Some assumptions were made in this procedure: the methyl group has C_{3v} symmetry and

∠H-C-H=109.5°, r(C-H)=1.091 Å, and ∠N=C=Se=180°. Table 4 shows the assumed and derived structural parameters. If the estimation error of r(C=Se) from the similar molecules is ±0.010 Å, the errors of r(C-N), r(N=C), and ∠C-N-C are ±0.009 Å,

Table 1. Observed Rotational Transitions(MHz) of $CH_3NC^{80}Se$ in the Ground State

Transition	$CH_3NC^{80}Se$	
	ν_{obsd}	$\Delta\nu$[a]
3_{22}—2_{21} } 3_{21}—2_{20} }	9858.74	−0.14
3_{03}—2_{02}	9860.80	0.14
3_{12}—2_{11}	9874.15	0.14
4_{14}—3_{13}	13128.61	0.07
4_{13}—3_{12}	13165.51	0.18
5_{15}—4_{14}	16410.79	0.15
5_{14}—4_{13}	16456.60	−0.02
6_{16}—5_{15}	19692.61	−0.11
6_{06}—5_{05}	19721.25	0.07
6_{15}—5_{14}	19747.69	−0.21
7_{62}—6_{61} } 7_{61}—6_{60} }	22970.66	−0.03
7_{17}—6_{16}	22974.71	−0.06
7_{53}—6_{52} } 7_{52}—6_{51} }	22982.09	0.01
7_{44}—6_{43} } 7_{43}—6_{42} }	22991.43	−0.01
7_{35}—6_{34} } 7_{34}—6_{33} }	22998.71	0.03
7_{26}—6_{25} } 7_{25}—6_{24} }	23003.89	0.04
9_{19}—8_{18}	29538.58	−0.20
9_{37}—8_{36} } 9_{36}—8_{35} }	29569.39	−0.14
9_{28}—8_{27} } 9_{27}—8_{26} }	29576.16	−0.01
9_{09}—8_{08}	29581.52	0.08
9_{18}—8_{17}	29621.53	−0.02
$10_{1,10}$—$9_{1,9}$	32820.70	−0.02
$10_{3,8}$—$9_{3,7}$ } $10_{3,7}$—$9_{3,6}$ }	32854.71	−0.19
$10_{2,9}$—$9_{2,8}$ } $10_{2,8}$—$9_{2,7}$ }	32862.32	0.05
$10_{0,10}$—$9_{0,9}$	32868.21	0.10
$10_{1,9}$—$9_{1,8}$	32912.73	0.04
$11_{1,11}$—$10_{1,10}$	36102.70	0.08
$11_{3,9}$—$10_{3,8}$ } $11_{3,8}$—$10_{3,7}$ }	36140.40	0.18
$11_{2,10}$—$10_{2,9}$ } $11_{2,9}$ —$10_{2,8}$ }	36148.50	0.17
$11_{0,11}$—$10_{0,10}$	36154.80	0.07
$11_{1,10}$—$10_{1,9}$	36203.62	−0.17
$12_{1,12}$—$11_{1,11}$	39384.37	−0.11
$12_{3,10}$—$11_{3,9}$ } $12_{3,9}$ —$11_{3,8}$ }	39425.49	0.02
$12_{2,11}$—$11_{2,10}$ } $12_{2,10}$—$11_{2,9}$ }	39433.60	0.26
$12_{0,12}$—$11_{0,11}$	39441.11	−0.19
$12_{1,11}$—$11_{1,10}$	39494.78	−0.06

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

Table 2. Observed Rotational Transitions(MHz) of $CH_3NC^{78}Se$ in the Ground State

Transition	$CH_3NC^{78}Se$	
	ν_{obsd}	$\Delta\nu$[a]
6_{16}—5_{15}	19836.68	0.01
6_{06}—5_{05}	19865.33	−0.05
7_{17}—6_{16}	23142.76	0.06
9_{19}—8_{18}	29754.52	−0.14
9_{37}—8_{36} } 9_{36}—8_{35} }	29785.60	−0.04
9_{28}—8_{27} } 9_{27}—8_{26} }	29792.50	0.13
9_{09}—8_{08}	29797.70	0.01
$10_{1,10}$—$9_{1,9}$	33060.47	−0.10
$10_{3,8}$—$9_{3,7}$ } $10_{3,7}$—$9_{3,6}$ }	33095.00	−0.01
$10_{2,9}$—$9_{2,8}$ } $10_{2,8}$—$9_{2,7}$ }	33102.30	−0.17
$10_{0,10}$—$9_{0,9}$	33108.37	−0.01
$10_{1,9}$—$9_{1,8}$	33153.26	−0.09
$11_{1,11}$—$10_{1,10}$	36366.30	−0.13
$11_{3,9}$—$10_{3,8}$ } $11_{3,8}$—$10_{3,7}$ }	36404.30	−0.02
$11_{2,10}$—$10_{2,9}$ } $11_{2,9}$ —$10_{2,8}$ }	36412.54	−0.02
$11_{0,11}$—$10_{0,10}$	36419.11	−0.10
$12_{1,12}$—$11_{1,11}$	39672.44	0.20

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

Table 3. The Observed and Calculated Rotational Constants for CH_3NCSe

	$CH_3NC^{80}Se$		$CH_3NC^{78}Se$	
	Obsd	Calcd[a]	Obsd	Calcd[a]
A/GHz	100 (50)		100[b]	
	102.700[c]		102.908[c]	
B/MHz	1648.045 (8)	1647.92	1660.104 (8)	1659.92
C/MHz	1638.848 (8)	1638.87	1650.826 (8)	1650.76
Δ_J/kHz	0.180 (23)		0.204 (28)	
Δ_{JK}/kHz	74.05 (28)		75.00 (48)	

Figures in parentheses indicate the uncertainty attached to the last figures, estimated from 2.5 times the standard deviations.

a) Calculated from the structural parameters in Table 4. b) Assumed. c) Calculated from assuming the inertia defect(−3.2 amuÅ^2).

Table 4. Structural Parameters of CH_3NCSe

Assumed parameters	Derived parameters
r(C-H) : 1.091 Å	r(C-N) : 1.447±0.009 Å
r(C=Se) : 1.708 Å	r(N=C) : 1.205±0.010 Å
∠H-C-H : 109.5 Å	∠C-N-C : 157.0±4.0°
∠N=C=Se : 180°	

Table 5. Comparison of the Structural Parameters(Å) for Similar Molecules

	r(C-N)	r(N=C)	r(C=Se)	R-N-C(deg)
CH_3-NCSe[a]	1.447	1.205	(1.708)	157.0
CH_3-NCS	1.452[b]	1.216[b]		147.46[b]
	1.4123[c]	1.2068[c]		152.52[c]
CH_3-NCO	1.437[b]	1.207[b]		139.98[b]
	1.4342[d]	1.207[d]		140.18[d]
H-NCSe[e]		1.195	1.717	143.0
H-NCS[f]		1.207		131.7
H-NCO[g]		1.214		123.9
CH_2=C=Se[h]			1.706	
S=C=Se[i]			1.695	
O=C=Se[j]			1.7098	

a) This work, b) Ref. 4, c) Ref. 9, d) Ref. 8, e) Ref. 1, f) Ref. 7, g) Ref. 6, h) Ref. 11, i) Ref. 12, j) Ref. 13, ( ): assumed.

±0.010 Å, and ±4° respectively. The rotational constants calculated from the derived structural parameters are consistent with the observed ones, as shown in Table 3.

The derived values of the bond lengths, r(C-N) and r(N=C), are in agreement with those of similar molecules within less than 0.01 Å, as shown in Table 5. The angle of C-N-C of 157° is much larger than the ones of CH_3NCO and CH_3NCS. A similar trend is seen for the case of the H-N-C angle in HNCO (124°), HNCS(132°), and HNCSe(143°).

References

1) B. M. Landsberg, *Chem. Phys. Lett.*, **60**, 265 (1979).
2) T. Sakaizumi, Y. Kohri, O. Ohashi, and I. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **51**, 3411 (1978); B. M. Landsberg, *Z. Naturforsh.*, **33a**, 1323 (1978); T. Sakaizumi, M. Obata, T. Takahashi, E. Sakaki, O. Ohashi, and I. Yamaguchi, *Bull. Chem. Soc. Jpn.*, to be published.
3) W. J. Franklin, R. L. Werner, and R. A. Ashby, *Spectrochimica Acta*, **30A**, 1293 (1974).
4) R. G. Lett and W. H. Flygare, *J. Chem. Phys.*, **47**, 4730 (1967).
5) S. Nakagawa, S. Takahashi, T. Kojima, and C. C. Lin, *J. Chem. Phys.*, **43**, 3583 (1965).
6) K. Yamada, *J. Mol. Spectrosc.*, **79**, 323 (1980).
7) K. Yamada, M. Winnewisser, G. Winnewisser, L. B. Szalanski, and M. C. L. Gerry, *J. Mol. Spectrosc.*, **79**, 295 (1980).
8) J. Koput, *J. Mol. Spectrosc.*, **106**, 12 (1984).
9) M. Kreglewski, *Chem. Phys. Lett.*, **112**, 275 (1984).
10) R. E. Schuster, J. E. Scott, and J. Casanova, Jr., *Org. Synth.*, **V**, 772 (1973).
11) B. Bak, O. J. Nielsen, H. Svanholt, and A. Holm, *Chem. Phys. Lett.*, **55**, 36 (1978).
12) C. Hirose and R. F. Curl, Jr., *J. Chem. Phys.*, **55**, 5120 (1971).
13) M. W. P. Strandberg, T. Wentink, and A. G. Hill, *Phys. Rev.*, **75**, 827 (1949).