

# Microwave Spectrum and Structure of Silyl Isothiocyanate

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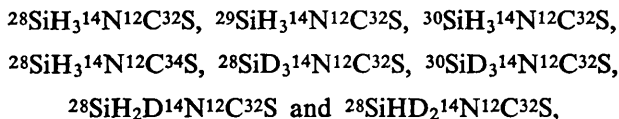
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The microwave spectra of eight isotopic forms of silyl isothiocyanate,  $\text{SiH}_3\text{NCS}$ , have been recorded, from which the  $C_{3v}$  symmetry of the molecule is established and the structural parameters found to be  $\text{Si}-\text{N} = 1.714 \pm 0.010 \text{ \AA}$ ,  $\text{N}-\text{C} = 1.211 \pm 0.010 \text{ \AA}$ ,  $\text{Si}-\text{H} = 1.489 \pm 0.010 \text{ \AA}$ ,  $\text{H}-\text{Si}-\text{H} = 111^\circ 22' \pm 10'$ , with  $\text{C}-\text{S} = 1.560 \text{ \AA}$  (assumed). The centrifugal distortion constant  $D_{JK}$  is evaluated for the most abundant forms of  $\text{SiH}_3\text{NCS}$ ,  $\text{SiH}_2\text{DNCS}$ ,  $\text{SiHD}_2\text{NCS}$  and  $\text{SiD}_3\text{NCS}$  as 41.9, 40.5, 37.0 and 31.4 kc/sec respectively. The spectrum of  $\text{SiH}_3\text{NCS}$  in the first excited state of its lowest frequency vibration has also been measured and the rotational, rotation-vibration, and centrifugal distortion constants determined. A rough estimate of the frequency, which involves bending of the  $\text{SiNCS}$  chain, of  $54 \text{ cm}^{-1}$  is made.

In a previous paper<sup>1</sup> it was established that the substance produced by the reaction between silyl iodide and silver thiocyanate is the isothiocyanate,  $\text{SiH}_3\text{NCS}$ , rather than the thiocyanate,  $\text{SiH}_3\text{SCN}$ . A fairly detailed molecular structure was deduced by combining results of infra-red and microwave measurements.

The present investigation was undertaken in order to extend the observations of rotational constants to the isotopic forms,



from which a more accurate molecular structure may be deduced. A further object was to study the rotational transitions of molecules in the first excited state of a skeletal bending vibration, the frequency of which appears to be very low.

## EXPERIMENTAL

Measurements were made over the region 18,000-36,500 Mc/sec with a Stark modulation spectrometer described previously.<sup>2</sup> The frequency measurements, based on the National Physical Laboratory, Rugby, 5 Mc/sec transmission, are accurate to within 0.1 Mc/sec in general, except for weak lines with unresolved fine structure, which may be rather more in error.

The silyl isothiocyanate was stored at liquid-nitrogen temperature, since it decomposed on standing in bulk at room temperature for extended periods. It was allowed to come to room temperature for very brief periods for sampling. It was found necessary to condition the absorption cell with several samples of the vapour, after which the spectrum remained unchanged for some hours at room temperature.

Observations were made between  $-80^\circ\text{C}$  and room temperature, the optimum temperature being intermediate and determined by the vapour pressure. The intensities of lines ranged up to about  $10^{-5} \text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

SPECTRUM AND MOLECULAR STRUCTURE FOR GROUND  
VIBRATIONAL STATE

The fully symmetric forms—those with  $\text{SiH}_3$  or  $\text{SiD}_3$ —gave spectra characteristic of symmetric tops. The transition  $(J+1) \rightarrow J$  is split into  $K+1$  lines, with  $K = 0, 1, \dots, J$ , fitting the well-known formula

$$\nu = 2(J+1)(B_0 - D_{JK}K^2) - 4D_J(J+1)^3,$$

where  $D_{JK}$  and  $D_J$  are centrifugal distortion constants  $\ll B_0$ . Plots of  $\nu$  against  $K^2$  enable values of  $B_0$ ,  $D_{JK}$  and  $D_J$  to be obtained, given that more than one value of  $J$  is considered. An example of the fit between experimental data and those for the best straight line is given in table 1 for the  $J = 8 \leftarrow 7$  transition of  $^{28}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$ . All lines with  $K \neq 0$  have large first-order Stark shifts. The line with  $K = 0$ , which has a second-order Stark shift, requiring higher fields, was not clearly

TABLE 1.—OBSERVED AND BEST-FIT CALCULATED FREQUENCIES  
FOR THE  $J = 8 \leftarrow 7$  TRANSITIONS OF  $\text{SiH}_3\text{NCS}$ ,  $\text{SiH}_2\text{NCS}$   
AND  $\text{SiHD}_2\text{NCS}$  (MOST ABUNDANT ISOTOPES OF Si, N, C AND  
S). VALUES IN Mc/sec

(i)  $\text{Si}_3\text{HNCS}$ 

$K$	obs.	calc.
0	—	24256.29
1	24255.75	24255.62
2	24253.81	24253.61
3	24250.15	24250.25
4	24245.53	24245.56
5	24239.39	24239.52
6	24232.05	24232.14
7	24223.56	24223.42

(ii)  $\text{SiH}_2\text{DNCS}$ 

$K$	obs.	calc.
0	—	23665.36
{1	23698.48	23698.48
{1	23630.62	23630.62
2	23662.43	23662.77
3	23659.41	23659.53
4	23655.15	23655.00
5	23649.25	23649.17
6	23642.29	23642.05
7	23633.38	23633.64

(iii)  $\text{SiHD}_2\text{NCS}$ 

$K$	obs.	calc.
0	—	23113.84
{1	23147.76	23147.76
{1	23078.48	23078.48
2	23111.59	23111.47
3	23108.25	23108.51
4	23104.24	23104.37
5	23099.36	23099.04
6	23092.61	23092.54
7	23084.74	23084.82

seen. Where possible, the transition origin (i.e.,  $\nu$  for  $K = 0$ ) was found graphically, and the results are shown in table 2. For some of the less abundant isotopic species, the resolution of the lines was less clear against the background noise, and the characteristic intensity pattern, in which lines with  $K = 3, 6 \dots$  are strong because of the presence of identical nuclei, was of help in obtaining a (rather less accurate) transition origin.

TABLE 2.—ROTATIONAL PARAMETERS OF SILYL ISOTHIOCYANATE

species	transition	transition origin ( $K = 0$ ); (Mc/sec)	$B_0$ (Mc/sec)	$C_0$ (Mc/sec)
$^{28}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$	6 $\leftarrow$ 5	18192.17	1516.018 $\pm 0.008$	—
	7 $\leftarrow$ 6	21224.56		
	8 $\leftarrow$ 7	24256.29		
	10 $\leftarrow$ 9	30320.35		
$^{29}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$	8 $\leftarrow$ 7	23894.22	1493.389 $\pm 0.012$	—
$^{30}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$	8 $\leftarrow$ 7	23550.43	1471.902 $\pm 0.315$	—
$^{28}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{34}\text{S}$	8 $\leftarrow$ 7	23573.42	1473.39 $\pm 0.063$	—
$^{28}\text{SiD}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$	9 $\leftarrow$ 8	25423.26	1412.403 $\pm 0.023$	—
	8 $\leftarrow$ 7	22598.75		
$^{30}\text{SiD}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$	9 $\leftarrow$ 8	24786.84	1377.047 $\pm 0.028$	—
$^{28}\text{SiH}_2\text{D}^{14}\text{N}^{12}\text{C}^{32}\text{S}$	8 $\leftarrow$ 7	23665.36	1483.326 $\pm 0.025$	1474.844 $\pm 0.025$
$^{28}\text{SiHD}_2^{14}\text{N}^{12}\text{C}^{32}\text{S}$	8 $\leftarrow$ 7	23173.84	1448.947 $\pm 0.033$	1440.283 $\pm 0.033$

The characteristic effect of very slight asymmetry in  $\text{SiH}_2\text{D}$  or  $\text{SiHD}_2$  type molecules is the splitting of the  $K = 1$  transition into two widely spaced lines, the remaining values of  $K$  giving lines which fit the symmetric top formula well,  $B_0$  now being replaced by  $\frac{1}{2}(B_0 + C_0)$ . Fits based on the  $K = 1$  lines are shown in table 1 for the  $J = 8 \leftarrow 7$  transition for the most abundant forms of  $\text{SiH}_2\text{DNCS}$  and  $\text{SiHD}_2\text{NCS}$ . The derived values for the rotational parameters  $B_0$  and  $C_0$  are given in table 2. The parameter  $A_0$ , associated with rotation about the figure axis, cannot be determined directly from these spectra.

The first definite conclusion from the accurately symmetric top behaviour of the  $\text{SiH}_3$  and  $\text{SiD}_3$  molecules is the linearity of the Si—N—C—S chain. That the atoms are in this sequence is known from the earlier work.<sup>1</sup>

Following Costain's method<sup>3</sup> of determining distances from Kraitchman's equations<sup>4</sup> the distance  $r_s$  ( $^{28}\text{Si}$ —C. of G.) in  $^{28}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$  is found to be 2.2605 Å, calculating from the results for  $^{28}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$  and  $^{28}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{34}\text{S}$ . Substituting  $^{30}\text{Si}$  for  $^{29}\text{Si}$  leads to 2.2623 Å for the same quantity, giving a mean value of 2.2614 Å. A similar treatment of  $^{28}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{32}\text{S}$  and  $^{29}\text{SiH}_3^{14}\text{N}^{12}\text{C}^{34}\text{S}$  gives  $r_s$  ( $^{32}\text{S}$ —C. of G.) = 2.2242 Å. It would have been desirable similarly to place the carbon atom, but the necessary observations on lines of the  $^{13}\text{C}$ -containing species were not possible because of rather low sensitivity and interference from Stark components of neighbouring lines. The C—S distance has, therefore, been taken to be 1.560 Å, as found in  $\text{HNCS}$ ,<sup>5</sup>  $\text{CH}_3\text{NCS}$ <sup>6</sup> and  $\text{OCS}$ .<sup>7</sup>

Kraitchman's equations, derived for a plane asymmetric rotor, may be utilized to determine the position of a hydrogen atom in the molecule being studied here,

by choosing as a plane of reference that containing the SiNCS chain and the hydrogen atom undergoing substitution by deuterium, from SiH<sub>3</sub>NCS to SiH<sub>2</sub>DNCS (most abundant isotopes of Si, N, C and S). Solution of these equations then gives the co-ordinates of that hydrogen atom with respect to the centre of gravity.

It is necessary to insert values of  $I_A^0$ , the moment of inertia about the figure axis of the SiH<sub>3</sub> compound, and of  $\Delta I_A^0$ , the amount by which it changes on mono-deuterium substitution, in order to obtain solutions. Fortunately, the expressions are not very sensitive to the magnitude of  $I_A^0$ , and a value of 6.040 a.u. Å<sup>2</sup>, corresponding with 1.485 Å for Si—H bond length and 111° for the HSiH bond angle, was used. These approximate figures are based on recent work on silyl halides.<sup>8</sup>  $\Delta I_A^0$  is obtained from the relation  $\Delta I_A^0 = \Delta I_B^0 - \Delta I_C^0$ , which holds apart from a small deviation due to inertial defect.

The solution leads to more accurate values for  $r_s$  (Si—H) of 1.488 Å and HSiH angle of 111° 22'. Repetition of the process with  $I_A^0$  based on these figures gave no further change.

A similar procedure was followed with SiD<sub>3</sub>NCS and SiHD<sub>2</sub>NCS (most abundant isotopes), having placed the <sup>28</sup>Si atom in the SiD<sub>3</sub> compounds by considering it with respect to substitution by <sup>30</sup>Si. This gave values of  $r_s$  (Si—D) of 1.491 Å and DSiD angle 111° 22'.

The difference between the two values of the bond length may be ascribed to the use of Kraitchman's equations, which strictly apply only to rigid molecules, whereas the  $r_s$  values, which lie between the non-vibrating values ( $r_e$ ) and the zero-point vibration values ( $r_0$ ), are influenced by the vibration of the molecule. They thus depend to some extent on the particular isotopic forms used in the elucidation of the structure.

By use of the first moment equation about the centre of gravity and the results derived above, together with the single assumption that the C—S distance is 1.560 Å, it is now possible to obtain a complete structure for the molecule, given in table 3. The estimated errors in table 3 arise not from the accuracy of measurement of the lines, which is much greater, but from the uncertainty of identification of  $r_s$  values derived by the Kraitchman-Costain method with the equilibrium values  $r_e$ .

The distortion constant  $D_J$  is very small (<0.3 kc/sec), but  $D_{JK}$  is significant. For SiH<sub>3</sub>NCS, SiH<sub>2</sub>DNCS, SiHD<sub>2</sub>NCS, SiD<sub>3</sub>NCS (most abundant isotopic species) it takes the values 0.0419, 0.0405, 0.0370, 0.0314 (all  $\pm 0.001$ ) Mc/sec respectively. This order is in general agreement with the expectation that distortion constants are proportional to  $B^2/\omega$ , where  $\omega$  represents a vibration frequency, and hence to (reduced mass)<sup>-3/2</sup>.

TABLE 3.—STRUCTURE OF SILYL ISOTHIOCYANATE

$r$ (C—S) = 1.560 Å (assumed)
$r$ (N—C) = 1.211 Å
$r$ (Si—N) = 1.714 Å
$r$ (Si—H) = 1.489 Å
H—Si—H angle = 111° 22' $\pm$ 10'
All distances are $\pm 0.010$ Å.

#### MOLECULES IN EXCITED VIBRATIONAL STATES

A large number of groups of lines were observed which were ascribed to vibrationally excited molecules. The most interesting of these were a series of at least five groups of lines on the high-frequency side of each ground-state rotational transition. These groups were roughly equally spaced from the ground-state group, and diminished steadily in intensity away from that group. Their intensities at room temperature and -80°C were such as to indicate a vibrational frequency below 100 cm<sup>-1</sup>. It should be noted that one of the degenerate bending frequencies has not

been detected in infra-red<sup>9</sup> and Raman studies down to  $100\text{ cm}^{-1}$ , and it is reasonable to suppose that it is this one, known as  $\nu_{10}$ , which is responsible for these groups of lines.

If the strongest feature of each group is used as a basis of measurement then a rough value of  $\alpha_{10}$ , the rotation-vibration coupling constant may be obtained for up to 5 vibrational quanta from the approximate formula,

$$B_v = B_0 - n\alpha_{10},$$

where  $n = 1, \dots, 5$ . These values are  $-10.4$ ,  $-10.2$ ,  $-10.0$ ,  $-9.8$  and  $-9.6$  Mc/sec respectively for successive increasing values of  $n$ .

An accurate evaluation of  $\alpha$  for all these states must await a detailed theory of the structure of the transitions for  $n > 1$ . For  $n = 1$ , a suitable theory has been propounded by Nielsen.<sup>11</sup> A doubly degenerate bending vibration is associated with an internal angular momentum ( $l\hbar/2\pi$ ), with a component ( $\zeta\hbar/2\pi$ ) about the molecular axis of symmetry, where  $|\zeta| \leq 1$  and is not expected to be far from unity. In the first excited vibrational state  $l = \pm 1$ . The angular momentum about the molecular axis due to rotation of the molecular framework is now  $A_v(K - \zeta l)^2$  or approximately  $A_v(K - l)^2$ .

The case  $K = l = \pm 1$  now produces two relatively widely spaced lines ( $l$ -type doublet), with the same spacing  $\Delta\nu_1$  as for the first excited state of a degenerate bending vibration of a linear molecule,

$$\Delta\nu_1 = 2q(J+1),$$

where  $q$  is called the  $l$ -type doubling constant. The levels with, e.g.,  $K = \pm 4$ ,  $l = \pm 1$  and  $K = 2$ ,  $l = \mp 1$ , which have the same value of  $|K - \zeta l|$  with  $\zeta = 1$ , also give rise to a doublet, as do other combinations which obey the same condition.

The centres of the doublets, according to Nielsen,<sup>11</sup> are at frequencies  $\nu_c$  given by

$$\nu_c = 2B_v(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1) - 2D_{JK}\bar{K}^2(J+1) + 4(2D_J + D_{JK})(J+1)\zeta,$$

where  $B_v$ ,  $D_{JK}$ ,  $D_J$  refer to the vibrationally excited molecule and  $\bar{K}$  is the mean value of  $|K|$  for the two lines of a doublet. It is reasonable to assume that  $D_J$  is too small to affect the  $J = 8 \leftarrow 7$  transitions of  $\text{SiH}_3\text{NCS}$  on the basis of the ground state measurements so that

$$\frac{\nu_c}{2(J+1)} = B_v - D_{JK}\{1 + \bar{K}^2 + 2\zeta\}$$

and a plot of  $\nu_c$  against  $1 + \bar{K}^2$  should give  $D_{JK}$  and  $B_v - 2D_{JK}$ . The results give satisfactory linear plots, from which

$$D_{JK} = 41.5 \pm 1.0 \text{ kc/sec, and } B_v = 1526.28 \pm 0.01 \text{ Mc/sec (given } \zeta = 1.0).$$

The corresponding  $\alpha$ , obtained by subtracting  $B_0$  from  $B_v$ , is  $10.26 \pm 0.02$  Mc/sec. It should be noted that the value of  $D_{JK}$  is within experimental error the same as for the unexcited molecule.

As expected, the whole group of lines for the first excited state was made up of widely spaced doublets with two additional lines which were ascribed to  $K = l = \pm 1$ . These latter gave a value of  $q = 2.83 \pm 0.05$  Mc/sec. The detailed figures for the  $J = 8 \leftarrow 7$  transition of  $\text{SiH}_3\text{NCS}$  (most abundant isotopes) are given in table 4.

The separation  $\Delta\nu$  of doublets apart from  $K = l = \pm 1$  may be represented by a formula,

$$\Delta\nu = 8(J+1)\bar{K}[2\zeta D_J - (1 - \zeta)D_{JK} + \varepsilon\zeta] + \frac{2(J+1)\{(J+1)^2 - \bar{K}^2\}}{\bar{K}} \left( \frac{q^2}{4\{(1 - \zeta)A_v - B_v\}} \right)$$

This expression, apart from the term  $\epsilon\zeta$ , is due to Nielsen. The extra term, in which  $\epsilon$  is an empirical positive constant, was found to be necessary to fit the data for methyl cyanide.<sup>12</sup> It is formulated in this way so as to make the expression homogeneous in  $\zeta$ .

TABLE 4.—THE  $J = 8 \leftarrow 7$  TRANSITION OF  $\text{SiH}_3\text{NCS}$  IN THE VIBRATIONAL STATE  $\nu_{10} = 1$

$K$		obs. (Mc/sec)	calc. (Mc/sec)
$\pm 1$	$\pm 1$	$\begin{cases} 24444.32 \\ 24399.00 \end{cases}$	$\begin{cases} 24444.28 \\ 24398.96 \end{cases}$
$\pm 2$	$\pm 1$	$\begin{cases} 24420.40 \\ 24422.33 \end{cases}$	$\begin{cases} 24421.14 \\ 24422.02 \end{cases}$
$\pm 3$	$\pm 1$	$\begin{cases} 24419.31 \\ 24418.65 \end{cases}$	$\begin{cases} 24419.44 \\ 24418.56 \end{cases}$
$\pm 4$	$\pm 1$	$\begin{cases} 24416.85 \\ 24414.46 \end{cases}$	$\begin{cases} 24416.84 \\ 24414.70 \end{cases}$
$\pm 5$	$\pm 1$	$\begin{cases} 24412.92 \\ 24409.80 \end{cases}$	$\begin{cases} 24412.86 \\ 24409.64 \end{cases}$
$\pm 6$	$\pm 1$	$\begin{cases} 24406.83 \\ 24403.55 \end{cases}$	$\begin{cases} 24407.54 \\ 24403.32 \end{cases}$
$\pm 7$	$\pm 1$	$\begin{cases} 24401.33 \\ 24396.19 \end{cases}$	$\begin{cases} 24401.96 \\ 24395.70 \end{cases}$

A plot of  $(\Delta\nu/\bar{K})$  against  $(\bar{K})^{-2}$  is a straight line, within experimental error. Its slope should be

$$\frac{2(J+1)^3 q^2}{4\{(1-\zeta)A_v - B_v\}}$$

and is equal to  $-3.00 \pm 0.10$  Mc/sec.  $B_v$  and  $q$  are known, and if  $A_v$  is taken to be the same as  $A_0 = 69,200$  Mc/sec, then  $\zeta = 0.99 \pm 0.01$ , which is very satisfactory. Measurement of the intercept gives  $1.0 \pm 0.1$  Mc/sec, and leads to  $\epsilon\zeta$  being much the largest term in the bracket in which it occurs.

#### GENERAL

The following points are noteworthy about the structure presented in table 3. First, the linearity of the SiNCS chain indicates that the "lone pair" of the nitrogen atom must be incorporated into a hybridized state which gives bonding with the  $3d$  orbitals of the silicon atom. In consequence the Si—N bond is expected to be shorter than that obtained by adding the Pauling single bond radii for the two atoms. This addition gives  $1.87 \text{ \AA}$ , and the observed length is  $1.714 \text{ \AA}$ , in agreement with expectation. It may be compared with the SiN bond length in trisilylamine,<sup>13</sup>  $(\text{SiH}_3)_3\text{N}$ , of  $1.73 \pm 0.02 \text{ \AA}$ , where a similar bonding effect will be expected.

Secondly, the N—C distance of  $1.211 \text{ \AA}$  is not significantly different from the values it takes in the HCNS<sup>5</sup> and  $\text{CH}_3\text{NCS}$ <sup>6</sup> molecules. This supports the assumption of C—S =  $1.560 \text{ \AA}$ .

Thirdly, the parameters of the  $\text{SiH}_3$  group are quite similar to those found in recent work on the silyl halides. In these compounds, Si—H varies from  $1.473 \text{ \AA}$  in  $\text{SiH}_3\text{F}$  to  $1.488 \text{ \AA}$  in  $\text{SiH}_3\text{I}$ . The HSiH angle appears to be about  $\frac{1}{3}^\circ$  larger than in the halides.

The final point concerns the low-frequency bending vibration. Use of the relationship,<sup>14</sup>  $q \sim 2B_0^2/\omega$  gives a frequency  $\omega$  of  $54 \text{ cm}^{-1}$ , with the  $q$  value obtained above in agreement with the intensity considerations which suggest a frequency

below  $100\text{ cm}^{-1}$ . It may be noted that this bending frequency has not been observed in recent infra-red<sup>9</sup> and Raman<sup>10</sup> work where a lower frequency limit of the observations did not extend as far as this.

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