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INFRARED SPECTROSCOPIC AND DIELECTROMETRIC INVESTIGATION OF THE MOLECULAR GEOMETRY OF ISOCYANATO- AND ISOTHIOCYANATO-SILANE DERIVATIVES

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Summary

The molecular geometry of compounds of the series $(CH_3)_nSi(NCX)_{4-n}$, (where $n = 0, 1, 2, 3$ $X = S, O$) were investigated with the objective of determining the magnitudes of the Si—N—C angles. Measurements of the infrared spectra and dipole moments were carried out. The infrared spectra unambiguously suggest linearity, and this is supported by dipole moment calculations. The deviation from linearity observed by electron diffraction is a consequence of shrinkage effects δ(Si—N—C—X) resulting from low frequency, large amplitude vibrations. From the dipole moment values it is concluded that the N—Si—N angle in the di- and trifunctional isothiocyanates is larger than the tetrahedral angle. The structural differences between the silicon and carbon compounds can be attributed to $(d-p)\pi$ bonding in the former.

Introduction

Numerous papers have dealt with the geometrical aspects of isocyanato- and isothiocyanato-silane molecules [1—5,7,8]. There is controversy over the configuration of the Si—N—C—X (X = S, or O) chains.

Table 1 summarizes the relevant data. There is a striking difference between microwave spectroscopic results indicating linear chains and electron diffraction findings indicating a highly bent structure. Both of these techniques yielded bent structures for the carbon analogs (methyl-isocyanate and methyl-isothiocyanate). Although considerations of the physical meaning of the structural information yielded by these two techniques resolve the apparent contradictions concerning the structures the silicon derivatives (see Discussion), we decided to extend the structural information on these compounds by infrared spectroscopic and dielectrometric studies, and the results are described below.

TABLE 1

VALUES OF Si—N—C AND C—N—C ANGLES FOR VARIOUS ISOCYANATO AND ISOTHIOCYANATO DERIVATIVES

Compound	θ (°)	Method	Literature
H_3SiNCO	180	MW	[1]
	151.7	ED	[1]
F_3SiNCO	160.7	ED	[1]
Cl_3SiNCO	158.0	ED	[2]
$(CH_3)_3SiNCO$	150	ED	[3]
$Si(NCO)_4$	180	IR/Ra	[4]
	146.4	ED	[5]
H_3CNCO	140	MW	[6]
H_3SiNCS	180	MW	[7]
	163.8	ED	[8]
$(CH_3)_3SiNCS$	154	ED	[3]
$Si(NCS)_4$	172.5	X	[8]
H_3CNCS	147.5	MW	[6]

MW = microwave spectroscopy, ED = electron diffraction, X = X-ray, IR/Ra = infrared and Raman spectroscopy.

TABLE 2

ASSIGNMENTS OF INFRARED SPECTRA OF ISOCYANATO-DERIVATIVES

Compound	$(CH_3)_3SiNCO$	$(CH_3)_2Si(NCO)_2$	$CH_3Si(NCO)_3$	$Si(NCO)_4$	$(CH_3)_3CNO$
Assignment	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
ν_{as} CH_3	2970s	2980m	2980w	—	2982m
ν_s CH_3	2912m	2920w	2928w	—	2888w
$\nu_{SiN} + \nu_{as}$ NCO	2815w	2795w	2798w		—
ν_{as} NCO	2290vs	2360vs 2280vs	2340vs 2285vs	2285vs	2258vs
ν_s NCO	1445m	1455s	1464m	1474m	1468s
δ_{as} CH_3		1413m	1418m	—	1398m
δ_s CH_3	1380vw	1390vw		—	1373m
$\delta_s(Si)CH_3$	1263s	1273s	1268s	—	—
$\nu_{C(CH_3)_3}$	—	—	—	—	1240s 1200s
ν_{C-C}	—	—	—	—	851s
$\delta_{as}(Si)CH_3$	850vs	845m	812vs	—	—
$\delta_s(Si)CH_3$	768s	825s	—	—	—
ν_{C-N}	—	—	—	—	711m
ν_{as} SiC	698m	715m	670s	—	—
ν_s SiC	645s			—	—
δ_{NCO}	624s	626vs 591vs	615vs 550m	614vs	621vs 592vs
ν_{Si-N}	532s	528m	518m	544m	—
δ_{C-C}	—	—	—	—	452s

TABLE 3

ASSIGNMENTS OF INFRARED SPECTRA OF ISOTHIOCYANATO-DERIVATIVES

Compound	$(CH_3)_3SiNCS$	$(CH_3)_2Si(NCS)_2$	$CH_3Si(NCS)_3$	$Si(NCS)_4$	$(CH_3)_3CNCS$
Assignment	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
ν_{as} CH_3	2972w	2974w	2980w	—	2988s
ν_s CH_3	2908vw	2911vw	2918vw	—	2882w
$\nu_{SiN} + \nu_{as}$ NCS	2528vw	2560vw			—
ν_{as} NCS	2090vw	2105s 2075vs 2013s	2082s 2038m	2095s 2082m	2103vs
δ_{as} CH_3	1417w	1405w	1415w	—	1470m
δ_s CH_3	1335vw		1330vw	—	1378m
$\delta_s(Si)CH_3$	1262s	1268m	1278s	—	—
$\nu_C(CH_3)_3$	—	—	—	—	1270m 1215s
ν_s NCS	960vs	1090vs 1025vs	1120vs 1050vs	1094vs	998s
2 × δ_{NCS}		970m	920m	935m	
ν_{as} CN	—	—	—	—	885m
ν_{C-C}	—	—	—	—	858m
$\delta_{as}(Si)CH_3$	850s	835m	788s	—	—
$\delta_s(Si)CH_3$	766m	818s	—	—	—
ν_{as} SiC	708m	693m		—	—
ν_s SiC	637vs			—	—
δ_{NCS}	483m	482s	460s	470s	522s 492s
ν_{SiN}	438s 555vw?	442s	440s	430w 598vw?	—

Experimental

The compounds $(CH_3)_nSi(NCO)_{4-n}$ were prepared by the method of Forbes and Anderson [9]. The compounds $(CH_3)_nSi(NCS)_{4-n}$ were made by Voronkov and Dolgov's method from the methyl-chlorosilanes by reaction with silver cyanate or from tetrachlorosilane by treatment with ammonium thiocyanate. The purities of the products were checked by various analytical methods.

Investigations by infrared-spectroscopy

The infrared spectra of the derivatives were recorded with a Zeiss UR-20 spectrometer. The methyltri(isothiocyanato)silane and the tetra(isothiocyanato)silane are solids at 298 K, and their spectra were recorded as KBr-discs, while the spectra of the liquid derivatives were obtained using KBr cells, with cooling to avoid decomposition.

Tables 2 and 3 present the assignments.

Dielectric measurements

The dielectric constants of the members of the two series $(CH_3)_nSi(NCO)_{4-n}$

TABLE 4

MEASURED DIPOLE MOMENTS

Compound	Dipole moment (10^{-29} Cm)	
	using Hedestrand's method	using Onsager's method
$(CH_3)_3CNCO$	0.96	
$(CH_3)_3SiNCO$	0.92	0.91
$(CH_3)_2Si(NCO)_2$	1.00	
$CH_3Si(NCO)_3$	0.89	0.88
$Si(NCO)_4$	0.31	0.32
$(CH_3)_3CNCS$	1.01	
$(CH_3)_3SiNCS$	1.07	
$(CH_3)_2Si(NCS)_2$	1.06	
$CH_3Si(NCS)_3$	0.79	
$Si(NCS)_4$	0.38	

and $(CH_3)_nSi(NCS)_{4-n}$ (where $n = 0, 1, 2, 3$) and the two carbon analogues, tert-butyl isocyanate and tert-butyl isothiocyanate were investigated by Hedestrand's [11] method using cyclohexane as solvent. In a few cases Onsager's [12] solvent-free method was also utilized. The dielectric constants were obtained using a WTW Dipolmeter 01. Table 4 lists the measured dipole moments.

Results and discussion

Infrared spectroscopy

Colthup [13] gives a range of 1395—1375 cm^{-1} for the ν_s(NCO) frequency, while we found it in the range 1474—1445 cm^{-1}. For ν_s(NCS) of alkyl-isothiocyanates Colthup gives the range 700—650 cm^{-1}; we found at this frequency in the spectra of the isothiocyanato silanes a very strong band between 1094—960 cm^{-1}. The ν_s(NCS) band of tert-butylisothiocyanate also falls in this range (at 998 cm^{-1}).

Our results agree with those of Thayer and Strommen [14], who investigated the infrared spectra of trimethyl-isocyanato- and trimethyl-isothiocyanato derivatives of the Group IVA elements. We concluded from their results that the deformational vibration of the isothiocyanate group is in the range of 522—480 cm^{-1} and that of the δ(NCO) between 626—591 cm^{-1}. This is supported by results obtained by Koster [15] who found the δ(NCO) vibration of tert-butylisocyanate at 627 cm^{-1} and the δ(NCS) vibration of trichlorosilylisocyanate at 469 cm^{-1}. The ν(Si—N) band was found for the isocyanate derivatives in the range 544—518 cm^{-1}, and for isothiocyanates in the range 442—430 cm^{-1}.

There is no agreement in the literature about the assignment of the Si—N stretching frequency. According to Cyvin et al. [16], the δ(NCS) band in H_3SiNCS is at 497 cm^{-1}, and this is supported also by theoretical calculations. At the same time they suggest assigning the 555 cm^{-1} frequency to ν(SiN), but Ebsworth [17] assigned the 497 cm^{-1} band as a ν(Si—N) vibration and the band 555 cm^{-1} as a combinational frequency. From our spectra we agree with Cyvin on the δ(NCS) assignment, but we could not unambiguously assign the 555

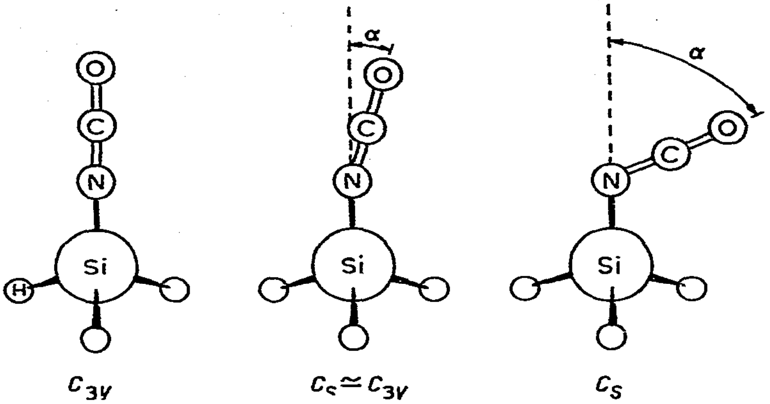

Fig. 1. Molecular symmetry in the case of H_3SiNCO.

cm^{-1} frequency, of very low intensity, which occurs only for the trimethylsilyl isothiocyanate. (Note the question-mark by that frequency in Table 3.) There are similar difficulties in the case of the tetra(isocyanato)- and tetra(isothiocyanato)-silanes. According to Carlson [18] and Miller [19] the ν(Si—N) stretching frequency of tetra-isothiocyanatosilane appears at 598 cm^{-1}, and that of (tetraisocyanato)silane at 727 cm^{-1}. In our spectrum of $Si(NCS)_4$ a weak band was observed at the frequency 598 cm^{-1}, but this cannot be safely assigned as a ν(Si—N) vibration.

If the ν(Si—N) vibration was in the 600—550 cm^{-1} range for isothiocyanato derivatives, then the corresponding vibration for the isocyanato compounds would appear in a higher frequency range.

We did observe a vibration of medium intensity at 727 cm^{-1} in the spectrum of $Si(NCO)_4$, but this did not show up in the spectra of the other isocyanatosilanes. Thus Thayer and Strommen's assignment of the ν(Si—N) stretching frequency as 520 cm^{-1} seems more likely, and we assumed this in making our assignments. The assignments for di- and trifunctional compounds show good agreement with those for mono- and tetrafunctional derivatives.

In the case of tert-butyl compounds we were able to assign both the ν(C—C) and ν(C—N) bands.

The Si—N—C angle in the isocyanato- and isothiocyanato-silane derivatives can be best studied with the monofunctional compounds. The structures considered for H_3SiNCO, the simplest silane derivative, are shown in Fig. 1. If the angle Si—N—C is 180°, then the molecule belongs to the C_{3v} point group. If the skeleton is bent by the angle α, the symmetry decreases to C_s, in this case the degeneracy of the vibration of type e disappears (and there is separation into a' and a'' species). However, if the value of α is not too large, then the a' and a'' bands do not separate sufficiently to be resolved, and the absence of degeneracy does not provide certain evidence for a linear skeleton. (Pseudosymmetry.) Splitting of the bands on the other hand does provides evidence for the non-linear skeleton. In the case of $(CH_3)_3MNCX$ molecules (where M = C, Si; X = S, O) the number of normal frequencies is 42, of which 15 are characteristic of the A_3MNCX skeleton.

TABLE 5

VIBRATIONAL MODES AND SYMMETRY CLASSES

Pointgroup	C_{3v}	$C_s \sim C_{3v}$	C_s
Fundamentals	15	15	15
IR-active	15	15	15
Species	5 a_1 5 e	10 a—5 a_1 5 a''—5 e	10 a 5 a''

Table 5 represents the number and type of the normal vibrations of the skeleton for C_{3v} and C_s symmetry.

It will be seen that when the symmetry is C_{3v} only 10 bands can be observed, while for C_s symmetry 15 can be observed. All of them are infrared and Raman active.

Tables 6 and 7 show the assignments of the skeleton of the derivatives $(CH_3)_3MNCX$ (M = C, Si; X = S, O).

It will be seen that for the tert-butyl compounds the vibrations ν(C—C), δ(NCX) and δ(C—C_3) are split, showing clearly that the C—N—C angles in both cases show a definite deviation from 180°, while in silicon compounds there is no deviation from the C_{3v} symmetry. This was also indicated by Goubeau and Reyhing [20] on the basis of Raman spectra of isothiocyanates, where the vibrations ν_{as}(Si—C) 706 cm^{-1} and δ_{as}(Si—C_3) 151 cm^{-1} also show no splitting.

Ebsworth [17], from studies of the high-resolution spectrum of H_3SiNCS, and Griffiths [21] from studies on H_3GeNCO, concluded that the skeleton

TABLE 6

ASSIGNMENTS OF INFRARED SPECTRA OF ISOTHIOCYANATO-DERIVATIVES
(skeleton vibrations only)

		C_s		C_{3v}			
		Frequency (cm^{-1})	Assignment	Assignment	Frequency (cm^{-1})		
c	1	2103	ν_{as} NCS	ν_{as} NCS	2090	1	a_1
	2	998	ν_s NCS	ν_s NCS	960	2	
	3	1215	νC—C	νSi—C	708	3	
	4	858	νC—C			4	
	5	885	νC—N	νSi—N	438	5	
	6	522	δNCS			6	
	7		δC—C_3			7	
	8		δC—C_3	δSi—C_3		8	
	9		$\delta(CH_3)_3CNCS$			9	
	10		δC—C—N			10	
a''	11	1270	νC—C	νSi—C	637	11	e
	12	492	δNCS	δNCS	483	12	
	13		δC—C_3	δSi—C_3		13	
	14		$\delta(CH_3)_3CNCS$	$\delta(CH_3)_3SiNCS$		14	
	15		$\delta C(CH_3)_3$	δSiNC		15	
		$(CH_3)_3CNCS$			$(CH_3)_3SiNCS$		

TABLE 7

ASSIGNMENTS OF INFRARED SPECTRA OF ISOCYANATO-DERIVATIVES (skeleton vibrations only)

		C_s		C_{3v}			
		Frequency (cm^{-1})	Assignment	Assignment	Frequency (cm^{-1})		
a	1	2248	ν_{as} NCO	ν_{as} NCO	2290	1	a_1
	2	1468	ν_s NCO	ν_s NCO	1445	2	
	3	1200	νC—C	ν_s Si—C	698	3	
	4	851	νC—C			4	
	5	711	νC—N	νSi—N	532	5	
	6	621	δNCO			6	
	7		δC—C_3			7	
	8		δC—C_3	δSi—C_3		8	
	9		$\delta(CH_3)_3CNCO$			9	
	10		δC—C—N			10	
a''	11	1240	νC—C	νSi—C	645	11	e
	12	592	δNCO	δNCO	624	12	
	13	452	δC—C_3	δSi—C_3		13	
	14		$\delta(CH_3)_3CNCO$	$\delta(CH_3)_3SiNCO$		14	
	15		$\delta(CH_3)_3C$	δSiNC		15	
		$(CH_3)_3CNCO$			$(CH_3)_3SiNCO$		

Si—NCS and Ge—NCS must be linear. If a linear skeleton is assumed for an MNCX group, the tetrafunctional derivatives possess T_d symmetry. The possible species are the following:

$3\,a_1 + 3\,e + 2\,t_1 + 6\,t_2$

Of these only the 6 t_2 frequencies are infrared active, if the MNCX skeleton of tetrafunctional derivatives is bent, then the symmetry of the molecule is decreased. In this case the highest symmetry of the molecule is D_{2d} ($6\,a_1 + 2\,a_2 + 3\,b_1 + 6\,b_2 + 8\,e$, of which 6 b_2 and 8 e are infrared active). For T_d symmetry 6 bands are expected, and for D_{2d} symmetry 14. Table 8 shows the classification for $Si(NCO)_4$ and $Si(NCS)_4$ compounds assuming T_d symmetry. It is evident that the Si—N—C skeleton must be linear or only slightly bent. Miller

TABLE 8

ASSIGNMENT OF INFRARED SPECTRA OF $Si(NCX)_4$ DERIVATIVES AT T_d SYMMETRY

Compound	$Si(NCO)_4$	$Si(NCS)_4$
Assignment	(cm^{-1})	(cm^{-1})
ν_{as} NCX	2285	2095
ν_s NCX	1474	1094
δ_{SiNCX}	614	470
ν_{Si-N_4}	544	430
δ_{SiNCX}		
δ_{SiN_4}		

and Carlson [19] reached the same conclusion for tetrafunctional isocyanato- and isothiocyanato-silanes and germanes.

The results for the trifunctional compounds are ambiguous. Both linear and bent structures can lead to C_{3v} symmetry, but a C_3 symmetry could also be due to twisting of —NCX groups around the N—Si bond. The spectra did not allow us to draw unambiguous conclusions on this point.

Dielectrometry

The fact that tetrafunctional compounds possess measureable dipole moments shows that the Si—N—C bond angle cannot be 180°.

In analysing the results, dipole moments were calculated by the method of group moments on the basis of different assumptions (I, II, III).

I. For first approximation we assumed, (in keeping with the electron diffraction result of Hjortaas [5]) that there is free rotation of NCO and NCS groups around the Si—N bond. Si—N—C bond angles were taken from the electron diffraction data, assuming the bent model. For our calculations we used a value of 154° for isothiocyanato-silanes and one of 150° for isocyanato derivatives [3].

Calculations were carried out using Eyring's equation [22] and relationships previously described [23].

Since the $m(\overrightarrow{\text{Si—N}})$ bond moment and the $m(\overrightarrow{\text{NCX}})$ group moment were not known, we determined them from the dipole moments of mono- and tetrafunctional compounds. The calculations give only the absolute value of the dipole moment, without any direction. However, the direction of $m(\overrightarrow{\text{Si—N}})$ moment is unambiguous, because the electronegativity difference between the atoms is so large that the negative pole must be the nitrogen. This could be compensated only to a small extent by any back-donation from the nitrogen atom.

There are various discussions in the literature about the direction of the m(NCX) moment. Entelis and Nesterov [24] concluded that the direction of the m(NCO) moment is opposite to that of $\overrightarrow{\text{RN}}$ in the organic compounds (RNCO, where R = H, CH_3), which means a direction $m(\overleftarrow{\text{NCO}})$. This conclusion was based primarily on the assumed value $\mu(\text{N—H}) = 0.47 \times 10^{-29}$ Cm (derived from the value for $\mu_{\text{N}(\text{CH}_3)_3}$ of 0.2×10^{-29} Cm.), and also on the decrease of the dipole moment on going from methylisocyanate (0.94×10^{-29} Cm) to isocyanic acid (0.53×10^{-29} Cm). Their observation that isothiocyanates possess larger dipole moments than isocyanates was in accord with the fact that the relative electronegativities ($\chi_O > \chi_S$) would cause $m(\overleftarrow{\text{NCO}})$ to be smaller than $m(\overleftarrow{\text{NCS}})$.

The m(NCS) moment in phenylisocyanates was assumed by Hunter and Partington [23] to be in the opposite direction [$m(\overrightarrow{\text{NCS}})$], and to have a value of 0.73×10^{-29} Cm. This assumption agrees with the results of dipole moment and NMR measurements made by Van den Berghe and Van der Kelen [26]. According to our calculations, if the vector m(NCX) is directed toward the nitrogen atom, the value of the $(\overrightarrow{\text{Si—N}})$ moment would have to be large (1.3—1.6×10^{-29} Cm.). Thus far on our further calculations $m(\overrightarrow{\text{NCX}})$ direction was used.

Our calculations for model I are summarized in the column I of Table 9. The differences between the calculated and experimental values are shown in parentheses. The bottom part of the column lists the calculated bond moments.

TABLE 9

MEASURED AND CALCULATED DIPOLE MOMENTS OF ISOCYANATO- AND ISOTHIOCYANATO-SILANE DERIVATIVES. CALCULATED BOND AND GROUP MOMENTS

Compound	Measured dipole moment (10^{-29} cm)	Calculated dipole moment (10^{-29} cm)		
		I	II	III
		$\Theta_{NCS} = 154°$ $\Theta_{NCO} = 150°$ Δ	$\Theta = 170°$ Δ	ν_{SiNCS} (cm^{-1}) = $2400\ \alpha^2$ ν_{SiNCO} (cm^{-1}) = $440\ \alpha^2$ ν_{SiNCO} (cm^{-1}) = $1090\ \alpha^4 - 300\ \alpha^2$
$(CH_3)_3SiNCS$	1.07	—	—	—
$(CH_3)_2Si(NCS)_2$	1.06	1.23 (0.17)	1.42 (0.36)	1.25 (0.19)
$CH_3Si(NCS)_3$	0.79	1.08 (0.29)	1.13 (0.34	1.12 (0.33)
$Si(NCS)_4$	0.38	—	—	—
$(CH_3)_3SiNCO$	0.92	—	—	—
$(CH_3)_2Si(NCO)_2$	1.00	1.09 (0.09)	1.18 (0.18)	1.07 (0.07)
$CH_3Si(NCO)_3$	0.89	0.96 (0.07)	0.92 (0.03)	0.94 (0.05)
$Si(NCO)_4$	0.31	—	—	—
$\overrightarrow{\mathrm{m(Si{-}CH_3)}}$		0.07	0.07	0.07
$\overrightarrow{\mathrm{m(NCS)}}$		0.43	1.09	0.65
$\overrightarrow{\mathrm{m(NCO)}}$		0.31	0.89	0.29 [a] 0.50 [b]
$\overrightarrow{\mathrm{m(Si{-}N)}}$		0.72	0.07	0.51 [c] 1.09 [a,d] 1.31 [b,d]

[a] Using anharmonic potential function; [b] using harmonic potential function; [c] in the case of NCS group; [d] in the case of NCO group.

It will be seen that every calculated dipole moment is larger than the measured values. (Excepted of course, for the mono- and tetrafunctional derivatives, which were used for calculations of group moments, and thus cannot show any such difference.) The deviation is large in the case of isothiocyanate compounds for the difunctional, especially the trifunctional derivatives. In keeping with this observation, we next supposed that the —NCO and —NCS groups lie in some definite direction in space, i.e. that rotation is hindered. This restriction can be accounted for on terms of the sizes of groups and of repulsion between the lone pairs of the nitrogen atoms. (Fig. 2.)

These space directions can be calculated on the basis of the known dipole-, group- and bond-moments. We assumed that the —NCX groups lie in the same direction and at the same angle. For the analysis the silicon atom was taken to be at the origin, with the z-axis bisecting the N—Si—N bond angle. The x—y plane is then determined by the N—Si—N atoms. The angles ϑ_0 shown in Table 10 represent the deviation from the z-axis, while the φ_0 angle refers to the angle enclosed by the x-axis and the projection of the —NCX group on the x—y plane.

This type of structure is supported by the Gergö, Hargittai and Schultz's

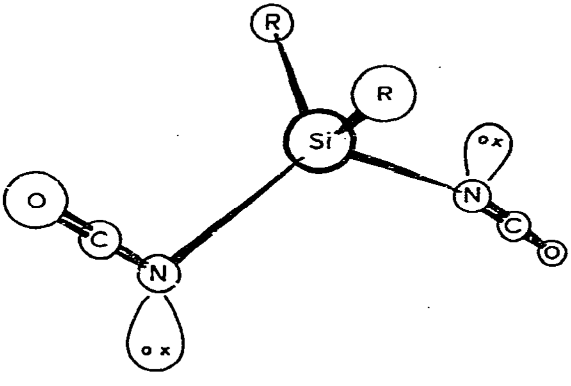

Fig. 2. The structure of $R_2Si(NCO)_2$ by bent Si—N—C angle.

analysis [27] of the molecular structure of methyltrimethoxysilane on the basis of the experimental results obtained by electron-diffraction for $(CH_3O)_3P{=}O$ by Oberhammer [28].

II. In the second model we assumed an Si—N—C angle deviating only to a small extent from linearity. A structure of this type is supported by various studies results, see e.g. Goubeau's conclusions [20,29] for organisilicon compounds on the basis of Raman spectra, and those of Murdoch and Rankin [30] for isocyanato-germanes from Raman-spectroscopy and électron-diffraction studies. Airey et al. [1] obtained a value of 172.5° for the Si—N—C angle in (tetraisothiocyanato)silane by X-ray diffraction.

In view of these results, we assumed the Si—N—C angle to be 170° for both isocyanato- and isothiocyanato-silane series. The dipole moments and bond moments caculated on this basis (assuming free rotation) are summarized in Column 2 of Table 9). It can be seen, that there are large differences from the experimental values.

III. For the third model we assumed the SiNCX group to be linear. This would conflict with the fact that the tetrafunctional derivatives possess a rather large dipole moment, and so we assumed the deformational vibration of Si—NCX to be of large amplitude and to be in the excited state at room-temperature; this could be responsible for the dipole moment of the tetrafunctional compounds. It is noteworthy that Glidewell and his co-workers [31] who find agreement between electron diffraction and microwave results for isocyanato-

TABLE 10

POLAR ANGLES OF —NCX VECTORS

Compound	X = O		X = S	
	ϑ_0	ϕ_0	ν_0	ϕ_0
$Si(NCX)_4$	104°28	24°06	107°34	21°19
$CH_3(NCX)_3$	104°57	31°06	96°20	23°04
$(CH_3)_2Si(NCX)_2$	113°26	31°51	110°44	24°35

and isothiocyanato-derivatives only with the aid of this assumption.

Since the deformation vibration δ(SiNCX) is of an *e* type, i.e. it is doubly degenerate, it may be concluded that it corresponds to an internal rotation. On this basis the "free rotational model" can be used. There are various published values for the δ(SiNCX) deformational vibration. Thus Cyvin [16] calculated the value of δ(SiNCO) as 69 cm^{-1}, and δ(SiNCS) as 113 cm^{-1}, Glidewell [31] for harmonic potentials derives value of 47 cm^{-1} and 100 cm^{-1} respectively, and for the anharmonic potential a value for δ(SiNCO) of 20 cm^{-1}, Durig [35] gives values of 29 cm^{-1} and 66 cm^{-1}, respectively. We have calculated an average dipole moment on the basis of the Boltzmann distribution with the aid of the potential function given Glidewell [31] and Durig [35], taking one excited level into account. It is of interest that this dipole moment is affected only to a negligible extent by the choice of potential function, and by taking more than one excited level into account.

Results calculated from the data of Glidewell are listed in the column 3 of Table 9. The dipole moment data of the isothiocyanate derivatives calculated by harmonic and anharmonic potential are essentially equivalent, and so are not separately listed. The values in Table 9 show clearly that the best results for the isocyanato series are obtained by use of model III.

The ratios of the dipole moments in tetrahedral molecules of the type A_nSiB_{4-n} (where $n = 1, 2, 3$) are 1,000 : 1,155 : 1,000, i.e. the dipole moments in the mono and trifunctional molecules should be the same, and those in the difunctional derivative should be the largest. In the isothiocyanato-series our measured values differ markedly from this ratio, so we assumed that the N—Si—N angle is larger than the tetrahedral value. Using model III, we obtained the following values for the N—Si—N angle:

$(CH_3)_2Si(NCS)_2$ 119,5°

$CH_3Si(NCS)_3$ 114,9°

In the light of the large size of the sulphur atom these values seem reasonable. Unfortunately, there are no structural data in the literature against which our findings can be tested.

Conclusions

Both the infrared spectra and the dipole moments indicate a linear structure for Si—N—C—X chains. A C_{3v} symmetry for monofunctional silicon compounds is unambiguously revealed by comparison with the carbon analogues, which have bent structures. The dipole moments of the tetrafunctional compounds result from the deformational vibrations having low frequencies and large amplitudes. That the Si—N—C angle differs significantly from the 180° indicated by electron diffraction measurements can be explained likewise (shrinkage-effect [16]). The difference between the structures of the silicon and carbon compounds can be attributed to the fact that the *d* orbitals of silicon take part in the bonding. Such $(p \rightarrow d)_\pi$ bonding is indicated by a shortening of the Si—N bond compared with the value calculated from Schomaker-Stevenson's rule [32]. This shortening is illustrated in Table 11 [33] for various isocyanato-derivatives.

TABLE 11

MEASURED AND CALCULATED X—N BOND LENGTHS

X	X—N bond length (Å)		
	measured	calculated	difference
Si	1.65—1.71	1.82	0.11—0.17
P	1.685	1.76	0.07
Cl	1.69—1.70	1.69	0.00—0.01
Ge	1.831	1.87	0.04
C	1.45	1.45	0.00

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