STRUCTURAL CHEMISTRY OF Si–H COMPOUNDS

E. A. V. EBSWORTH

University Chemical Laboratory, Cambridge, U.K.

The structural chemistry of SiH compounds is a vast topic. I shall touch on only a few aspects of its complexity in this lecture, which could be divided into two parts. The first part deals with some attempts to determine the geometry of molecular silicon compounds, and the second with the application of n.m.r. spectroscopy to some problems of silicon chemistry. In each of these fields, it is a real advantage to work with SiH compounds. In the determination of the structure of a molecule by almost any method, it is easiest to work with the simplest derivative possible; thus SiH_3-compounds are much easier to study than SiR_3-derivatives, whether by electron diffraction, microwave spectroscopy, or vibrational spectroscopy. In n.m.r., the resonance of H directly bound to Si should give more direct information about the other groups bound to silicon, because the proton is closer to the active site than are protons in alkyl groups attached to the silicon atom.

MOLECULAR GEOMETRY

The number of simple, volatile silicon compounds whose structures have been determined precisely is relatively small. Microwave spectroscopy has been used to determine bond distances and angles in the silyl halides, the trimethylsilyl halides, and a few asymmetric tops like Me_2SiH_2. Except in the simplest cases, however, it is almost always necessary to assume at least some of the parameters that are to be determined. Moreover, it is not as easy as it sounds to obtain the internuclear distances from the observed microwave lines, even in the simple silyl halides SiH_3X. The lengths of bonds from silicon to halogen or to carbon are well known by now, as is the fact that the SiF bond in the series $SiH_{3-n}F_n$ gets shorter as n increases, but the interpretation of the observed lengths in terms of the type of bonding is still rather subjective. It is interesting, of course, that Si–C bond lengths do not accord well with the idea of hybridization radii: the SiC bond lengths in silylacetylene[1] and in silyl cyanide[2] are appreciably different. Moreover, although the SiH angles and distances in these compounds have not been determined beyond question, it is clear from the values of the small moments of inertia obtained from the infrared spectra that the geometry of the SiH_3-group is appreciably different too[3]. It would be interesting but unfortunately difficult to find accurately the geometry of the Me_3Si-groups in Me_3SiCCH and in Me_3SiCN.

The silyl pseudohalides have also been studied by microwave spectroscopy. The spectrum of the isothiocyanate, SiH_3NCS, has been analysed in detail[4], but work is not yet complete on the spectra of silyl azide and silyl isocyanate. The spectrum of the isocyanate is complicated by the effects of centrifugal

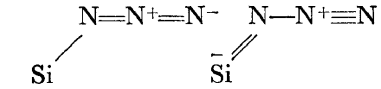
distortion and by the fact that there appears to be a bending vibration of the skeleton at ~ 30 cm^{-1}. The details of the structure are still uncertain, the more so since the N atom is very close to the centre of mass of the molecule; the molecular parameters that are at present believed to fit the spectrum best are shown in *Table 1*. It is certain that the SiO distance is rather shorter

Table 1. Molecular dimensions of some pseudohalides, MH_3NCX

Compound	*r*(MN) A	*r*(NC) A	*r*(CX) A	*r*(MH) A	HMH °	MNC °
HNCO[a]	0·99 ± 0·01	1·21 ± 0·01	1·17 ± 0·01	—	—	128°5′ ± 30′
CH_3NCO[b]	1·47 (ass)	1·19 ± 0·03	1·18 ± 0·03	1·09 (ass)	109·5° (ass)	125° ± 5°
SiH_3NCO[c]	1·699	1·150	1·179	1·506	110°24′	180°
HNCS[d]	0·989 ± 0·003	1·216 ± 0·007	1·561 ± 0·003	—	—	134°59′ ± 10′
CH_3NCS[e,g]	1·47	1·22	1·56	1·09	109°	142°
SiH_3NCS[f]	1·71 ± 0·01	1·21 ± 0·01	1·56 (ass)	1·49 ± 0·01	111°22′ ± 10	180°

[a] Ref. 5, [b] Ref. 6, [c] Ref.7, [d] Ref. 8, [e] Ref. 9, [f] Ref. 4.
[g] All parameters are apparently assumed.

than expected, but it is not clear which of the intervening bonds is relatively the shortest. Fortunately, though, the microwave spectra of symmetric tops differ sufficiently from those of even slightly asymmetric tops for it to be possible to say with certainty that silyl isocyanate is a symmetric top, with a linear heavy atom skeleton, and that silyl azide is not[10]; it has similarly been concluded that trimethylsilyl azide is an asymmetric top[11]. For silyl azide, this conclusion is reinforced by the absence of easily-resolved rotational detail in the infrared bands associated with SiH bending and stretching[12]. I know of no reason why such detail would not be resolved if the skeleton were linear, and indeed it is often observed even in slightly asymmetric tops (MeNCS)[13, 14]. These differences have been rationalized in valence bond terms[15]; while we usually associate the linearity of silyl isocyanate with $(p \rightarrow d)\pi$-bonding from N to Si, it should be noted that $(p \rightarrow d)\pi$-bonding is also possible in the bent azide, through structures such as



Although it would be possible in principle to determine the structures of disiloxane and disilyl sulphide by microwave spectroscopy, they have so far only been investigated by electron diffraction, which of course gives the wide angle of 144° in disiloxane[16] and the narrow one of 97° in the sulphide[17]. Apart from trisilylamine[18], very few other silicon compounds have been studied really precisely by electron diffraction, and less direct methods must often be used to find the angles. From the ^{15}NH coupling constant in the n.m.r. spectrum of $(Me_3Si)_2NH$, for instance[19], it is possible to calculate the Si–N–Si angle as 129°, using a formula derived empirically for organic amines and amides that relates J(^{15}NH) to the s-character in the NH bond[20]. Though this value is very reasonable, it represents little more than a good guess, because the theory on which it is based has not been at all

widely tested. It has been more common in the past to use vibrational selection rules as indices of molecular geometry. It is well known, for instance, that the vibrational spectra of disilyl sulphide[21] and of trisilylamine[22] are consistent with the bent structure for the one molecule and the planar structure for the other. Unfortunately, however, vibrational selection rules only tell us which bands are allowed; they do not tell us whether all the allowed bands will be strong enough to be observed. The spectra of trialkylsilyl compounds are sometimes rather complicated for a full analysis, and so we (in collaboration with Dr. L. A. Woodward) have measured the vibrational spectra of trisilyl phosphine, trisilyl arsine and trisilyl stibine, to see if the results give us any idea as to the shapes of the Si_3X skeletons. It is, of course, of some interest to see whether $(p \rightarrow d)\pi$-interactions between silicon and elements of the second, third and fourth groups of the periodic table are of stereochemical importance.

Before considering the observed spectra, a word is necessary about the vibrational selection-rules for the planar and for the pyramidal models of $(SiH_3)_3X$. There are three differences to which I shall make particular reference:

1. *For skeletal stretching modes*

In the planar model, both modes are Raman-active, but only the antisymmetric one is allowed in the infrared. For the pyramidal model, both modes are allowed in both effects.

2. *For the skeletal bending modes*

In the planar model, one of the two skeletal bending modes is active in the Raman and one is forbidden; both are allowed in the infrared. In the pyramidal model, both are allowed in both effects.

3. *For the SiH_3 bending modes*

Here the selection rules may depend on the rotational conformation of the SiH_3-groups. We analysed the spectrum of trisilylamine in terms of the point group C_{3h}; this allows three SiH_3 bending modes in the infrared, of which one is Raman-forbidden, and four others in the Raman. As the central atom gets larger, the SiH_3-groups are likely to rotate more freely unless the SiXSi angles change too, and freer rotation would probably lead to the appearance of fewer, rather than more bands. For a pyramidal molecule, the selection-rules are less stringent; more infrared bands would be expected, and all of them should have Raman counterparts. It is not entirely clear to me how the point group will be affected by almost free rotation of the SiH_3-groups.

These rules sound very helpful, but in practice they are less useful than they sound. Of the compounds studied, only trisilylamine is sufficiently volatile to give high pressures in a normal gas-cell for infrared spectroscopy; liquid-phase spectra are hard to obtain, and the spectra of solids are not generally governed by the same selection-rules that hold for the free molecules. The skeletal bending modes appear in a region of the spectrum that is notoriously hard to study in the infrared, and presents problems even in the Raman; we have been unable to record infrared spectra at frequencies lower than 250 cm^{-1}, and so have had to rely entirely on Raman spectra in relation to

point 2 above, even though it is clear that weak Raman lines close to the exciting line may possibly have escaped detection. The results that follow are therefore to some extent provisional.

Bearing all these points in mind, we may now look at a line diagram of the spectra of $(SiH_3)_3X$ at frequencies lower than 1000 cm^{-1} (*Figure 1*). For the

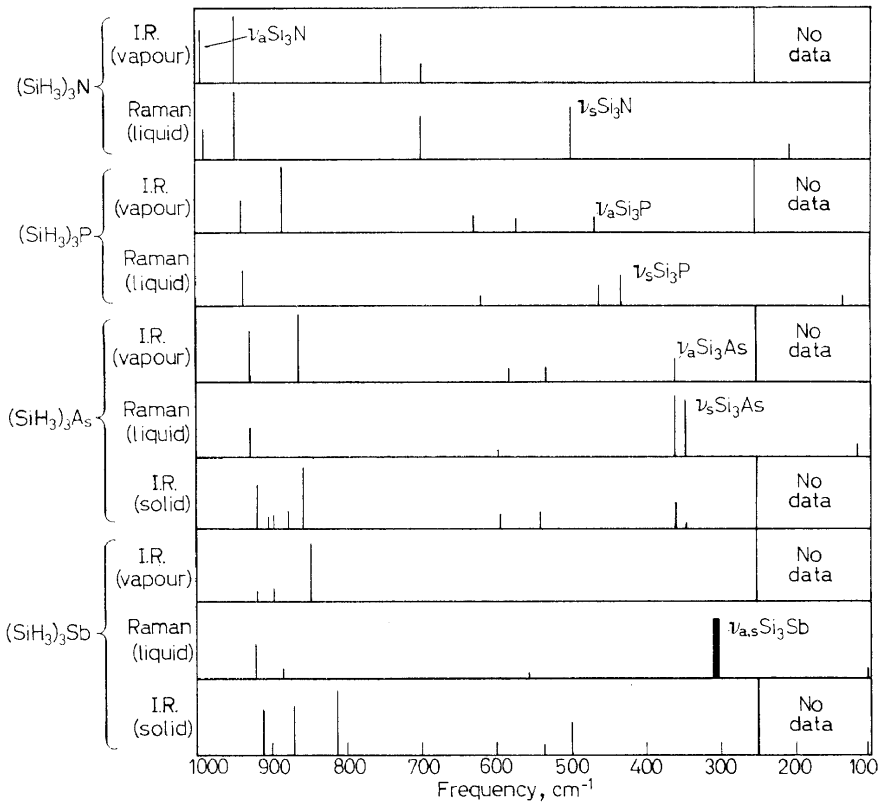


Figure 1. Approximate line drawing of the vibrational spectra of $(SiH_3)_3N$, $(SiH_3)_3P$, $(SiH_3)_3As$, $(SiH_3)_3Sb$; the phases are as stated

compounds of N, P and As, the skeletal stretching modes obey the selection rules for the planar model, so far as we can tell; the symmetric Si_3X stretching mode, which is present as a very weak band in infrared spectra of $(SiH_3)_3N$ at high pressures, is also present very weakly in the infrared spectra of solid $(SiH_3)_3P$ and $(SiH_3)_3As$, but we have not detected it in the infrared spectra of liquids or of the vapours (though I must admit that the spectrum we obtained of liquid $(SiH_3)_3P$ was not very satisfactory). Only one skeletal bending mode was observed in the Raman spectrum of the amine, the phosphine or the arsine; the SiH_3-bending modes of $(SiH_3)_3P$ and $(SiH_3)_3As$ give rise to two infrared bands, of which one (as predicted) has no Raman counterpart. All this is consistent with the planar structure for all three molecules, if we suppose coincidence of some of the SiH_3-bending modes; we could account for the spectra without difficulty in terms of slightly non-

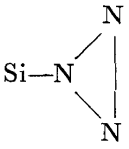
planar molecules, but it would be rather harder to do so if the Si—X—Si angles were close to the 100° of trialkyl phosphines. The stibine presents more of a problem. The observation of only one skeletal bending mode in the Raman implies a planar skeleton (unless, as is possible, the single Raman line represents two unresolved bands); on the other hand, there are at least three bands due to SiH_3 bending modes in the infrared spectrum, and the strongest of them (analogous to the band in the spectra of the phosphine and arsine with no Raman counterpart) in this case coincides with a weak Raman line. To make matters worse, the skeletal stretching modes are extremely weak in the infrared; we have only detected them as weak bands in the thickest of solid films, when the selection rules for the free molecules are not applicable. We can deduce little about the molecular geometry from our results in this case; Professor Amberger's results with the tris-trimethylsilyl compound are of great interest here. My own feeling is that the skeleton is further from planar for the antimony compound than for the others. It is perhaps worth noting that the Raman spectrum of trigermyl phosphine shows two skeletal bending modes in the Raman, indicating that the skeleton is not planar; the GeH_3 deformation modes in the infrared are split much as are the SiH_3 deformation modes of trisilyl antimony[23].

The main moral of all this is that while vibrational spectroscopy can give a clue as to the symmetry of a molecule, the method is unreliable, and the structure must ultimately be determined by some method such as electron diffraction or X-ray crystallography; we are making a crystallographic study of this particular series of compounds. Among examples where vibrational spectroscopy has led to the wrong conclusion about molecular symmetry, the best-known in silicon chemistry is of course the case of disiloxane[24], where the skeletal modes obey the selection rules for a linear model although the bond angle is 144°. Another, similar case is that of disilylcarbodiimide[25]. The infrared and Raman spectra of this compound are consistent with the molecule's having a linear SiNCNSi skeleton, but we do not observe rotational detail in the infrared spectrum; moreover, hexamethyldisilyl-carbodiimide had a substantial dipole moment[26], implying that a linear skeleton is not likely in this case at least. In general, the analysis of vibrational spectra leads more often to the attribution of too high a symmetry to a molecule than it leads to the attribution of a symmetry that is too low.

As for the influence of Si-methylation on the bond angles in silicon compounds, I am not convinced that any material differences have been conclusively demonstrated between Me_3Si- and H_3Si-compounds. There is some suggestion that the angles in Me_3SiO compounds and trimethylsilyl pseudohalides are rather narrower than in the corresponding H_3Si species, but I for one shall wait for more precise structural studies of the trialkylsilyl derivatives before coming to any decision on this point.

The wide angles from N, O or NCX to silicon are usually associated with $(p \rightarrow d)\pi$-bonding from nitrogen to silicon; I am not going to challenge this interpretation. If trisilyl phosphine and arsine are also planar, then we must conclude that $(p \rightarrow d)\pi$-bonding can also be stereochemically important between $3d$- and $3p$- or $4p$-orbitals. On the other hand, the non-linearity of silyl azide suggests that the factors that determine whether a lone pair is

stereochemically active or not are finely balanced; this is corroborated by the apparently very low skeletal bending frequencies in the linear silyl isocyanate and isothiocyanate. Perhaps the extent of delocalization of a lone pair necessary to make that lone pair stereochemically inactive is not large. It is only fair to point out, though, that we cannot exclude the structure



for silyl azide.

NMR SPECTROSCOPY

The proton resonance spectra of organosilicon compounds and silicon hydrides are of particular usefulness and importance, because, besides the usual ^{1}H chemical shifts and HH and ^{13}CH coupling constants, coupling is also observed with ^{29}Si in its natural abundance of 5 per cent. The^{29} Si satellites are much easier to find than ^{13}C satellites, and for H directly bound to ^{29}Si the fairly large coupling constants ($\sim$ 200–300 c/s) mean that at least one satellite is usually well clear of the main SiH resonances. The n.m.r. spectra may be used in at least three ways: to provide measurements for interpretation in terms of theoretical concepts and ideas about electronic structure; to identify groupings; or to afford rather more subtle information about molecular configurations and reactions. I propose to make a few comments about each of these headings in turn.

Theoretical explanation

At present, I do not feel that theories of chemical shifts or of coupling constants are advanced enough to make interpretations useful. Even for carbon compounds, the changes in the chemical shifts of α- or of β-hydrogen atoms are not so far as I know properly understood, and I do not know of any interpretation that is more satisfactory where alkyl-silicon compounds are concerned. The chemical shifts of hydrogen bound to silicon are even harder to understand. A semi-quantitative interpretation of the high-field shifts of hydrogen bound to transition metal atoms has been put forward[27], but to the best of my knowledge there is still no simple explanation for the low field shifts from CH_4 to SiH_4, GeH_4 and SnH_4, particularly since the shift from NH_4^+ to PH_4^+ appears to be to high field[28]. As far as coupling constants go, the coupling constants between nuclei directly bound together are dominated by the Fermi contact term, related to the *s*-character in the bonding orbitals[29]. This interpretation does not seem to be precisely defined enough, at least in silicon chemistry, to allow the calculation of bond angles from ^{29}SiH coupling constants (though I have already used this interpretation for ^{15}NH couplings!); none the less, it does at least provide a starting-point for the discussion of coupling constants between hydrogen and directly-bound ^{29}Si. The same is not true for couplings across more than one bond, such as $J(H—C—^{29}Si)$ in trialkylsilicon compounds. With these long-range couplings, it is essential to know the sign as well as the magnitude before attempting a theoretical analysis; a widely accepted theory of geminal

couplings, which was used by Dr Turner and myself[30] in an attempt to interpret HH couplings in substituted monosilanes, broke down completely when it was found to have predicted wrongly the signs of coupling constants whose magnitudes it had predicted with a fair degree of accuracy[31]. I am convinced by recent work, particularly by that of Dr Dreeskamp[32], to the extent that I believe both short and long range couplings are mainly determined by *s*-character; Professors Bothner-By and Pople have put forward a molecular orbital approach that looks encouraging[33]. But, unfortunately, in silicon chemistry the differences observed in couplings in related molecules are usually small, and none of these theories is yet capable of describing small differences adequately. As with so many chemical phenomena, the things measured represent small differences between large quantities. I therefore feel that it is more useful to look for correlations among n.m.r. parameters than to seek for explanations.

The identification of groupings

For the identification of new compounds, it is useful to have an idea of how the SiH chemical shifts change with substitution at silicon.

As *Table 2* shows, there is a low-field shift from $\tau(SiH_4)$, 6·81 p.p.m., with

Table 2. NMR parameters for some SiH compounds

	τ (p.p.m.)	J^{29}SiH (c/s)		τ^f (p.p.m.)	J^{29}SiH (c/s)		τ^f (p.p.m.)	J^{29}SiH (c/s)
SiH_3F[a]	5·24	229·0	$(SiH_3)_2O$[a]	5·39	221·5	$(SiH_3)_3N$[d]	5·57	213·9
			H_3SiOMe[e]	5·43		H_3SiNMe_2[d]	5·64	205·7
SiH_2F_2[a]	5·29	282 ± 3	$H_2Si(OMe)_2$[e]	5·55		$H_2Si(NMe_2)_2$[e]	5·62	217·6
$SiHF_3$[a]	5·49	381·7	$HSi(OMe)_3$[e]	6·02		$HSi(NMe_2)_3$[e]	5·87	235
SiH_3Cl[a]	5·41	238·1	$(SiH_3)_2S$[a]	5·65	224·0	$(SIH_3)_3P$[e]	6·08	211·4
SiH_2Cl_2[a]	4·60	288·0						
$SiHCl_3$[a]	3·97	362·9						
SiH_3Br[a]	5·83	240·5	$(SiH_3)_2Se$[a]	5·88	226	$(SiH_3)_3As$[e]	6·20	211·7
SiH_2Br_2[a]	4·83	289·0						
$SiHBr_3$[b]	3·69	357·0						
SiH_3I[a]	6·56	240·1				$(SiH_3)_3Sb$[e]	6·37	209·1
SiH_2I[a]	5·97	280·5						
$SiHI_3$[b]	5·51	325·1						

[a] Ref. 30, 34, [b] Ref. 35, [c] Ref. 36, [d] Ref. 37, [e] Ref. 38.
[f] τ measured in most cases in dilute solution in cyclohexane or tetramethylsilane as standard and solvent.

substitution of halogen, O, S, Se, N, P, As, Sb or C. This is like the pattern found in carbon chemistry. However, there is an important difference in the behaviour on further substitution. In methane, successive substitution of F, Cl, Br or I leads to a low-field shift[39]; the same is true for SiH resonances in chloro-, bromo-, iodo- or methyl derivatives of silane. With further substitution of F, O or N, however, the shift is very small indeed, and to high field. Why this should happen is not yet understood; it is tempting to associate the very small high field shifts on further substitution of these very electronegative elements with $(p \rightarrow d)\pi$-bonding, but I do not know of any justification for this interpretation; we must remember that the change in τ(SiH) from Me_2SiH_2 to Me_3SiH is only about −0·17 p.p.m.[40].

Methyl substitution in SiH_3X, SiH_2X_2 or $MeSiH_2X$ leads to a low-field

Table 3. Methyl substitution shifts of α-protons in silicon hydride compounds

Compound	*Methyl substitution shift*[a] (p.p.m.) F	Cl	Br	I	OR
$\overset{*}{SiH_3}X$	−0·03	−0·13	−0·32	−0·64	−0·06
$CH_3\overset{*}{SiH_2}X$	−0·04	−0·14	−0·31	−0·64	−0·06
$\overset{*}{SiH_2}X_2$	−0·05	−0·12	−0·44	−1·01	*b*
	SR	NR_2	CH_3	H	
$\overset{*}{SiH_3}X$	−0·17	−0·08	−0·26	−0·35	
$CH_3\overset{*}{SiH_2}X$	−0·18	−0·05	−0·04	−0·26	

[a] Methyl substitution shift = $\tau(CH_3\overset{*}{SiH}X—)—\tau(\overset{*}{SiH_2}X—)$, where X = F, Cl, Br, I, SR, NR_2, CH_3 or H. [b] Not measured.

shift in the SiH resonance; some data are presented to illustrate this in *Table 3*.

The proton resonance chemical shift of SiH_3-groups is to some extent characteristic of the other atom bound to silicon, and is much less sensitive to remote substitution. The SiH_3N resonance, for example, falls within a range of 0·14 p.p.m. in the 8 compounds studied, which makes the parameter of some diagnostic usefulness[40] (*Table 4*). But the range is overlapped by the

Table 4. Si*H* n.m.r. parameters in some SiH_3N compounds[a]

Compound	τ(p.p.m.)	$J(^{29}SiH)$ (c/s)
$(SiH_3)_3N$	5·56[a]	212
$(SiH_3)_2NMe$	5·56[a, c]	209
SiH_3NM_2	5·64[b]	205
SiH_3NCO	5·58[a]	231·5
SiH_3NCS	5·54[a]	240
SiH_3NCSe	5·51[a]	243·2
SiH_3N_3	5·51[a]	230·3
$(SiH_3)_2CN_2$	5·55[a]	225

τ for dilute solutions in: [a] cyclohexane; [b] CCl_4; [c] $SiMe_4$. Refs. 12, 41.

ranges that apply for SiH_3O-compounds at one end[34, 37] and for SiH_3S-compounds at the other[34, 42]; in fact, the last SiH_3O-compound in *Table 5*

Table 5. Si*H* n.m.r. parameters in some SiH_3O compounds[a]

Compound	τ(p.p.m.)	$J(^{29}SiH)$ (c/s)
$(SiH_3)_2O$	5·39[b]	221·5
SiH_3OMe	5·44[b]	
$HCOOSiH_3$	5·45[b]	234·9
$CH_3COOSiH_3$	5·53[b]	231·3
$CF_3COOSiH_3$	5·32[b]	242·1
$Me_2NCOOSiH_3$	5·54[c]	232·8

[a] Refs. 34, 37, 43.
[b] τ for dilute solutions in cyclohexane.
[c] τ for dilute solutions in $SiMe_4$

might from its n.m.r. parameters just as well contain SiH_3N. It is worth noting, incidentally, that the SiH_3O chemical shifts do not follow the normally accepted sequence of inductive properties of the other group attached to O; silyl acetate gives resonance to high field of methoxysilane. It is just possible that there is some interaction between the silicon atom of silyl acetate and the carbonyl oxygen, but the u.v. spectra of silyl and of methyl esters are very similar, at least for the vapour phase (the n.m.r. spectra were of course recorded in solution)[37].

As an illustration of the usefulness of $\tau(SiH)$ when combined with measurements of $J(^{29}SiH)$, *Table 6* shows the parameters obtained from mixtures of

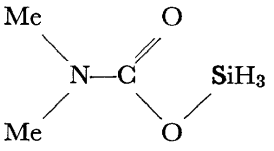
Table 6. N.m.r. parameters for SiH_3NMe_2 and for mixtures of this amine with CO_2, CS_2 and COS

Reactant	*Solvent/ standard*	τCH (± 0·05) (p.p.m.)	$J(^{13}CH)$ (± 0·5) (c/s)	τSiH (−0·03) (p.p.m.)	$J(^{29}SiH)$ (± 0·5) (c/s)
SiH_3NMe_2	95%, TMS	7·51	134·6	5·64	205·7
	5%, TMS	7·54	—	5·64	205·4
	5%, $CHCl_3$	7·55	—	5·71	206·9
SiH_3NMe_2/CO_2	CO_2, TMS	7·09	138·6	5·55	233·6
	CCl_4, TMS	7·07	—	5·54	232·8
SiH_3NMe_2/CS_2	CS_2, TMS	6·59	140·1	5·63	234·3
	CCl_4, TMS	6·52	—	5·65	—
SiH_3NMe_2/COS	CCl_4, TMS	6·78 6·66	—	5·39	235·9

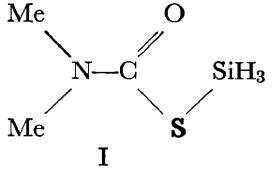
SiH_3NMe_3 with CO_2, CS_2 and COS. The products of these reactions are unstable at room temperature, even in vacuum, losing SiH_4, though they are rather more stable in CCl_4 solution; the reactions were allowed to occur in n.m.r. tubes at low temperatures, and the spectra showed that the amine and CO_2 react rapidly even at −46°. There are two or three interesting features about these spectra. The SiH resonances of the systems containing CO_2 or CS_2 are consistent with the formation of silyl carbamate (or thiocarbamate),

$$H_3SiX.C(X)NMe_2.(X=O \text{ or } X=S)$$

However, restricted rotation about the CN bond might be expected to lead to non-equivalent methyl groups; we must assume either that the rotational barrier is low enough to prevent the observation of splitting even at −46°, or that the molecule adopts a *cis*-configuration on which the N-methyl groups might be effectively equivalent:



For the product of the reaction with COS there are two possible structures:



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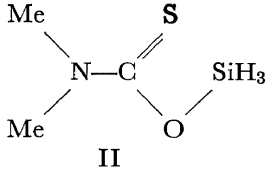


II

Rough calculations assuming a low value ($\sim$60 kcal) for E(SiS) suggest that the structure (II) should be preferred on grounds of energy. The n.m.r. spectrum shows only one SiH resonance, with only one set of satellites, so that the product is likely to be homogeneous; but the methyl proton resonance is split into two peaks of roughly equal intensity, whose splitting is unchanged between $-45°$ and room temperature. The SiH chemical shift is in the SiH_3O-region, but some 0·2 p.p.m. to low field of the lowest SiH_3S-resonance I know of (in SiH_3SCF_3)[42]; moreover, both CH_3 resonances are closer to $\tau(CH_3)$ in the CS_2 derivative than in the CO_2 compound, which seems to imply the presence of C=S rather than C=O. All this favours structure (II). The splitting of the methyl proton resonance, however, is a little odd. If the NMe-groups in the CO_2 and CS_2 derivatives are equivalent though rotational averaging, the barrier in the COS compound must be so much higher that such averaging is prevented even at $-40°C$; it is not immediately obvious why this should be so. If, however, rotation is restricted in all three, but the methyl groups in the other two compounds are equivalent through the *cis*-configuration of the XCXSi system, then it is easy to see why the methyl resonance in the derivative of COS is split; in this compound the two methyl groups would necessarily remain non-equivalent.

The use of ^{29}SiH satellites

These satellites are useful to the structural chemist in a number of ways, in addition to providing a valuable parameter for qualitative analysis.

In the detection of intermolecular interactions

First, they may be helpful in detecting intermolecular interactions. The coupling between directly bound nuclei decreases as the coordination number of one of the nuclei increases. For instance, $J(^{29}SiF)$ changes from 178 c/s in SiF_4 to 110 c/s in $SiF_6^=$. Thus changes in $J(^{29}SiH)$ with solvent should provide a useful way of investigating fairly weak interactions between SiH-compounds and donor solvents. Unfortunately, we have so far been unable to obtain solutions of the adducts of the bromo- or iodosilanes with bases that are concentrated enough for us to be able to detect the ^{29}SiH satellites; we believe that some at least of these adducts are ionic[35, 44], and $J(^{29}SiH)$ in species like $py_2SiH_3^+$ or $py_4SiH_2^{2+}$ would be of great interest. We do find, though, that J(29SiH) of SiH_3I dissolved in acetonitrile is very close to the value found for the same compound in cyclohexane as solvent, so solvation of SiH_3I by acetonitrile is unlikely to be strong.

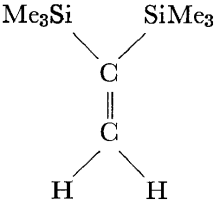
We have also investigated the interaction between monosilane and both pyridine and trimethylamine[35]. We have sealed enough SiH_4 in n.m.r. tubes with pyridine or with trimethylamine to give pressures over the liquid

(assuming no solubility) of 20–40 atm. at room temperature. The n.m.r. spectrum of SiH_4 shows no material change from that found in cyclohexane even down to temperatures as low as −82° (in the case of trimethylamine). We conclude that interaction between SiH_4 and either of these bases is at its strongest very weak, and we have found no evidence for any interaction at all. We have found no evidence that Me_3SiH forms an adduct with pyridine.

To indicate the pressure of more than one equivalent Si atom

In molecules containing more than one equivalent silicon atom, the presence of ^{29}Si will normally destroy the magnetic equivalence; for statistical reasons, the proportion of molecules containing more than one ^{29}Si atom is usually small. Thus, to take the simplest example, the spectrum of disilane[45] consists of a single sharp resonance, due to $(^{28}SiH_3)_2$, with widely spaced satellites due to $H_3{}^{29}Si^{28}SiH_3$ and closely-spaced satellites due to $H_3{}^{29}Si^{28}SiH_3$. The presence of the single ^{29}Si atom introduces an effective chemical shift between the two sets of protons of about (1/2)J, and as a result both sets of satellites appear as quartets (splitting 4·85 c/s) because of coupling between the two sets of protons. If longer-range coupling can be detected, it may provide valuable structural evidence as to the nature of the compound being studied. The main resonance of a 2 per cent (molar) solution of trisilylarsine[38], for example, was (as expected) a single line. The wide satellites, due to the ^{29}SiH protons of molecules $^{29}SiH_3As(^{28}SiH_3)_2$, were found to be split by the six equivalent ^{28}SiH protons into heptets, with internal spacing of 0·673 c/s, while the close satellites, due to the ^{28}SiH protons of $^{29}SiH_3As(^{28}SiH_3)_2$ coupling across As with the ^{29}Si atom, were further split by the three ^{29}Si–H atoms into quartets. This represents a conclusive proof of the structure of the compound as $(SiH_3)_3X$. Long-range coupling of this sort has so far been detected in the spectra of disilyl sulphide, trisilyl phosphine and (as above) trisilyl arsine.

A similar situation can arise in the spectra of compounds that do not contain SiH bonds. The olefinic resonance[46] of the compound



consists of a single sharp peak, because the two H atoms are equivalent. The ^{29}Si satellites, however, are more complex, because the presence of a single ^{29}Si atom destroys the equivalence of the olefinic protons—J(*cis*) $^{29}SiCCH$ and J(*trans*) $^{29}SiCCH$ are not quite the same. Thus the ^{29}Si satellites represent the AB part of an ABX spectrum, and six of the expected eight lines can be resolved.

The ^{29}Si satellites can also be used to simplify complex spectra in which protons bound to neighbouring silicon atoms have chemical shifts that are small compared with J(HH). The effective chemical shifts introduced by coupling with directly bound ^{29}Si are large enough to make it possible to

treat the satellites as first-order spectra. This is how the spectrum of trisilane was solved[43]; the main resonance is very complicated, but the satellites consist of overlapping triplets and heptets, from which (with a little fiddling) the parameters from which the main spectrum can be calculated are obtained.

The study of labile systems

Like most spectroscopic methods, n.m.r. may be used to investigate equilibrium systems without disturbing the equilibrium concerned; molar concentrations may be found using signal intensities, and if activity coefficients are ignored it is easy to calculate rough values of the equilibrium constant. We have been studying the systems

$$R_3Si(\text{or Ge})X + HY \rightleftharpoons R_3Si(\text{or Ge})Y + HX$$

where R is H or Me, and X is halogen. The spectra show that the equilibrium is set up at room temperature, and *Table 7* shows the equilibrium

Table 7. Apparent equilibrium constants for the reaction, $R_3MX + HY \rightleftharpoons R_3MY + HX$, at room temperature

R	M	X	Y	K (approx.)*
H	Si	Cl	Br	1
H	Si	Cl	I	0·05
H	Si	Br	I	0·1
H	Ge	Cl	Br	700
H	Ge	Cl	I	2600
H	Ge	Br	I	0·4
Me	Si	Cl	Br	0·1
Me	Si	Cl	I	0·005
Me	Si	Br	I	0·05

*Note that these are not *true* equilibrium constants, since the concentrations of the hydrogen halides were not measured.

constants we have obtained[47]. Where K is very small or very large, of course, the value is correspondingly approximate. Though rough calculations of ΔH (from bond energies) for all of these reactions suggests that K might be expected to be about 1, you can see that it is markedly different from 1 in some cases; in the silicon systems, HI is formed preferentially, and in the germyl systems, HCl. We have not yet determined K over a range of temperature, so we do not yet know whether the free energy changes are derived mainly from changes in ΔH or in ΔS. I mention this work, however, partly because of a peculiar effect we found in the germyl case. We studied the reaction between GeH_3X and HY in a variety of solvents; we find that the exchange of X with Y is much faster than the exchange of H with D if one uses GeH_3X and DY, so we conclude that the mechanism involving dissociation of GeH_3X into GeH_2 and DX is unlikely to be important. The spectra we obtained using as solvent tetramethylsilane that had been dried over molecular sieve at $-80°$ consisted of the expected sharp, separate GeH resonances at room temperature; but those obtained using the solvent dried over molecular sieve at room temperature gave a single broad GeH resonance at room temperature, mid-way between the positions of the resonances in GeH_3Br and GeH_3I (the system in which this effect is most easily

defined). This resonance split as the tube was cooled into two separate resonances, which were only slightly broadened at −80°; this all indicates rapid exchange of X with Y, suggesting that the lifetimes are about 0·01 sec. There is thus some catalyst for this system, but what the catalyst is we have no idea. It is not water, not chloroform, presumably not a base, not a Lewis acid. I myself suspect the surface of the glass, for we have not yet defined absolutely clearly the conditions under which rapid exchange is observed. I mention these results as an awful warning to anyone who tries to do kinetic work in these systems by n.m.r.

References

[1] J. S. Muenter and V. W. Laurie. *J. chem. Phys.* **39**, 1181 (1963).
M. C. L. Gerry and T. M. Sugden. *Trans. Faraday Soc.* **61**, 2091 (1965)
[2] J. Sheridan and A. C. Turner. *Proc. chem. Soc.* 21 (1960).
N. Muller and R. C. Bracken. *J. chem. Phys.* **32**, 1577 (1960).
[3] A. G. Robiette. *Ph.D. Thesis*, Cambridge University (1964).
[4] D. R. Jenkins, R. Kewley, and T. M. Sugden. *Trans. Faraday Soc.* **58**, 1284 (1962).
[5] L. H. Jones, J. N. Shoolery, R. G. Shulman and D. M. Yost. *J. chem. Phys.* **18**, 990 (1950).
[6] E. H. Eyster, R. H. Gilette, and L. O. Brockway. *J. Am. chem. Soc.* **62**, 3236 (1940).
[7] M. C. L. Gerry, T. M. Sugden, and J. C. Thompson. *Nature, Lond.* **211**, 846 (1966).
[8] R. Kewley, K. V. L. N. Sastry, and M. Winnewisser. *J. Molec. Spectrosc.* **10**, 418 (1963).
[9] C. I. Beard and B. P. Dailey. *J. Am. chem. Soc.* **71**, 929 (1949).
[10] E. A. V. Ebsworth, D. R. Jenkins, M. J. Mays, and T. M. Sugden. *Proc. chem. Soc.* 21 (1963).
[11] J. S. Thayer and R. West. *Inorg. Chem.* **3**, 889 (1965).
[12] E. A. V. Ebsworth and M. J. Mays. *J. chem. Soc.* 3450 (1964).
[13] S. Cradock. Unpublished observations.
[14] A. J. Costoulas and R. L. Werner. *Aust. J. Chem.* **12**, 601 (1959).
[15] J. W. Linnett. *Nature, Lond.* **199**, 168 (1963).
[16] A. Almenningen, O. Bastiansen, V. C. Ewing, K. Hedberg, and M. Traetteberg. *Acta Chem. Scand.* **17**, 2455 (1963).
[17] A. Almenningen, K. Hedberg, and R. Seip. *Acta Chem. Scand.* **17**, 2264 (1963).
[18] K. Hedberg. *J. Am. Chem. Soc.* **77**, 6491 (1955).
[19] E. A. V. Ebsworth and G. Rocktäschel. Unpublished work.
[20] G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts. *J. Am. chem. Soc.* **86**, 5564 (1964).
[21] H. Linton and E. R. Nixon. *J. chem. Phys.* **29**, 921 (1958);
E. A. V. Ebsworth, R. Taylor, and L. A. Woodward. *Trans. Faraday Soc.* **55**, 211 (1959).
[22] D. W. Robinson. *J. Am. chem. Soc.* **80**, 5924 (1958);
E. A. V. Ebsworth, J. R. Hall, M. J. MacKillop, D. C. McKean, and L. A. Woodward. *Spectrochim. Acta* **13**, 202 (1958);
H. Kriegsmann and W. Förster. *Z. anorg. allg. Chem.* **298**, 212 (1958).
[23] S. Cradock, G. Davidson, E. A. V. Ebsworth, and L. A. Woodward. *Chem. Commun.* 511 (1965).
[24] R. C. Lord, D. W. Robinson, and W. C. Schumb. *J. Am. chem. Soc.* **78**, 1327 (1956).
[25] E. A. V. Ebsworth and M. J. Mays. *Spectrochim. Acta* **19**, 1127 (1963).
[26] L. Birkofer, A. Ritter, and P. Richter. *Tetrahedron Lett.* 195 (1962).
[27] A. D. Buckingham and P. J. Stephens. *J. chem. Soc.* 2747, 4583 (1964).
[28] E. A. V. Ebsworth and G. M. Sheldrick. *8th European Conference on Molecular Spectroscopy*, Copenhagen (1965).
[29] H. M. McConnell. *J. chem. Phys.* **24**, 460 (1956);
M. Karplus and D. M. Grant. *Proc. natn. Acad. Sci. U.S.A.* **45**, 1269 (1959).
[30] E. A. V. Ebsworth and J. J. Turner. *J. chem. Phys.* **36**, 2628 (1962).
[31] C. N. Banwell and N. Sheppard. *Discuss. Faraday Soc.* **34**, 115 (1962).
[32] H. Dreeskamp. *8th European Conference on Molecular Spectroscopy*, Copenhagen (1965).
[33] J. A. Pople and A. A. Bothner-By. *J. chem. Phys.* **42**, 1339 (1965).
[34] E. A. V. Ebsworth and J. J. Turner. *J. phys. Chem.* **67**, 805 (1963).
[35] H. J. Campbell-Ferguson. *Ph.D. Thesis*, Cambridge University (1965).
[36] A. G. MacDiarmid. Personal communication.
[37] J. C. Thompson. *Ph.D. Thesis*, Cambridge University (1965).
[38] E. A. V. Ebsworth and G. M. Sheldrick. *Trans. Faraday Soc.* in the press.
[39] S. G. Frankiss. *J. phys. Chem.* **67**, 752 (1963).

[40] S. G. Frankiss. *Ph.D. Thesis*, Cambridge University (1963).
[41] E. A. V. Ebsworth and M. J. Mays. *J. chem. Soc.* 4879 (1961); 4844 (1962); 3893 (1963).
[42] A. J. Downs and E. A. V. Ebsworth. *J. chem. Soc.* 3516 (1960).
[43] B. Sternbach and A. G. MacDiarmid. *J. Am. chem. Soc.* **83**, 3384 (1961).
[44] H. J. Campbell-Ferguson and E. A. V. Ebsworth. *Chem. and Ind.* 301 (1965).
[45] E. A. V. Ebsworth and J. J. Turner. *Trans. Faraday Soc.* **60**, 256 (1964).
[46] E. A. V. Ebsworth, G. Fritz, and D. Kummer. Unpublished work.
[47] S. Cradock and E. A. V. Ebsworth. Unpublished work.