Nuclear Magnetic Resonance Spectra of Some Silyl and Trimethylsilyl Pseudohalides

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Proton, ^{13}C, ^{15}N, and ^{29}Si n.m.r. spectra have been recorded for $SiH_3(CN)$, $SiH_3(NCY)$ (Y = O, S, or Se), and $SiMe_3(CN)$ at room temperature or below, as has the ^{77}Se spectrum of $SiH_3(NCSe)$. The spectra show no sign of the presence of other isomers, nor of any intermolecular exchange that is fast on the n.m.r. time scale. The n.m.r. parameters are given, together with T_1 and nuclear Overhauser enhancement measurements, for $SiMe_3(CN)$ at three different temperatures. The spin-rotation contribution to relaxation appears to be dominant.

THE distinction between organic nitriles and isonitriles is well established; ' normal ' and ' iso-' thiocyanates are chemically distinct, although normal cyanates seem not to exist. In silicon chemistry there has been some controversy over this sort of isomerism. When silicon compounds such as SiR_3Cl are converted into $SiR_3(CN)$ the same product is obtained irrespective of the chemical route used. For $SiH_3(CN)$ [1] and $SiMe_3(CN)$ there is little doubt that the cyanide is bound to silicon through carbon; no significant evidence has been produced to suggest that $SiH_3(NC)$ is present in detectable concentrations in samples of the former compound. Features in the i.r.[2] and microwave [3] spectra of $SiMe_3(CN)$ have been interpreted as indicating the presence of a little $SiMe_3(NC)$ in the normal form at room temperature, and some transition-metal complexes have been postulated as containing the iso form as ligand.[4] It has been suggested [5] (almost certainly incorrectly [6]) that $GeH_3(NCO)$ contains small amounts of the normal form, and the possibility that $SiH_3(NCY)$ might exist in a mobile equilibrium with the iso form predominating has not been conclusively disproved.

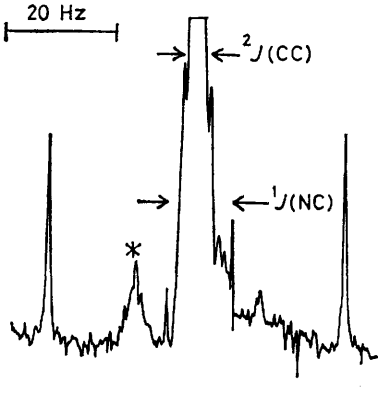
We have undertaken a study of the n.m.r. spectra of $SiMe_3(CN)$, $SiH_3(CN)$, and $SiH_3(NCY)$, where Y = O, S, or Se, to explore the possibility of fast intermolecular exchange and to see if we could detect any evidence for isomerism of any of these compounds in solution.

RESULTS

(*a*) $SiH_3(CN)$.—The ^1H n.m.r. spectrum of $SiH_3(CN)$, enriched to 95% with ^{15}N and to 90% with ^{13}C, in solution in CD_2Cl_2, consisted of a sharp doublet of doublets at room temperature; the ^{29}Si-$\{^1H\}$ spectrum also showed coupling to ^{13}C. No additional peaks were observed that could be due to $SiH_3(NC)$. The observation of couplings across the Si–C bond shows that fast intermolecular exchange does not occur under the conditions of the experiment. Cyclopentane solutions of the compound enriched only with ^{13}C showed similar couplings. Our failure to observe $^2J(SiN)$ in the ^{29}Si spectrum shows that it is small, certainly less than *ca.* 2 Hz. The n.m.r. parameters are collected in Table 1; the relative signs of coupling constants were obtained by various double-resonance (' tickling ') experiments, and absolute signs were then calculated assuming that the sign of $^1J(SiH)$ was negative.

(*b*) $SiH_3(NCY)$ (Y = O, S, *or* Se).—The ^1H n.m.r. spectra recorded at room temperature or at 233 K of these compounds enriched to 95% with ^{15}N and/or to 90% with ^{13}C consisted of sharp doublets or doublets of doublets; samples were prepared nominally containing ^{15}NCO, $N^{13}CO$, $^{15}N^{13}CS$, $^{15}NCSe$, or $^{15}N^{13}CSe$ groups, but the presence of 10% ^{12}C in the enriched-carbon samples allowed observation of signals from ^{15}N-only enriched species. The ^{29}Si-$\{^1H\}$ spectra also showed coupling to ^{15}N and ^{13}C as appropriate. There is thus nothing in the spectra to suggest that there is any intermolecular exchange that is fast on the n.m.r. time scale; we observed no peaks that could be assigned to other isomers. The n.m.r. parameters are collected in Table 1; relative signs of coupling constants and absolute signs were calculated as above.

(*c*) $SiMe_3(CN)$.—The ^1H spectrum of $SiMe_3(CN)$, 90% enriched in ^{13}C at CN, showed a doublet attributed to the $SiMe_3(^{13}CN)$ species, with spacing $|^3J(CH)|$ = 2.8 Hz; the CN region of the coupled ^{13}C spectrum was a decet consistent with this value of $|^3J(CH)|$. Moreover, the ^{13}C-$\{^1H\}$ spectrum displayed a doublet splitting in the methyl region due to two-bond C–C coupling, while the CN region showed satellite resonances corresponding to $|^1J(SiC)|$ = 53.3 Hz. All these observations make it quite clear that for the solutions we have studied there can be no fast exchange



^{13}C-$\{^1H\}$ N.m.r. spectrum of $SiMe_3(^{13}CN)$ (cyanide region only). The satellite peaks due to molecules containing ^{29}Si, ^{13}C at methyl, and ^{15}N are indicated. The peak marked with an asterisk is due to C_6D_6. Spectrometer conditions: acquisition time, 4 s; number of transients, 25

TABLE 1

N.m.r. chemical shifts (δ/p.p.m.) and coupling constants (J/Hz) for the compounds studied

Compound	δ(H)	δ(^{29}Si)	δ(^{13}C)	δ(^{15}N)	^1J(SiH)	^1J(SiN/C)	^1J(NC)	^2J(HN/C)	$\lvert ^2J$(SiC/N)$\rvert$	^3J(HC/N)
$SiMe_3(CN)$ [a]	0.069 [b]	−12.1	126.9	254.7		−53.3	11.6		1.6	+2.8
$SiH_3(CN)$	3.95	−87.4	118.35	258.9	−238	−62.5	−12.8	+4.9	(<2)	−1.4
$SiH_3(NCO)$	4.40	−58.1	123.7	−26.9	−234.9	+18.6	(−)46.3	−5.0	9.8	(+)2.6
$SiH_3(NCS)$	4.48	−59.73	143.61	50.18	−240.2	+16.8	−39.4	−4.2	7.1	+2.8
$SiH_3(NCSe)$ [c]	4.49	−53.53	142.17	78.3	−243.8	15.1	(−)34.1	(−)4.0	4.9	(+)2.8

Where signs of coupling constants are given without parentheses they are derived from double-resonance experiments on the assumption that ^1J(SiH) is negative in sign; signs in parentheses indicate relations between coupling constants not compared indirectly with ^1J(SiH) for the molecule concerned, but are inferred absolute signs by comparison with other molecules in the Table. Coupling constants for which no signs are indicated may have positive or negative sign, only the magnitudes being determined by our experiments.

[a] Other parameters: δ($^{13}CH_3$) = 1.8 p.p.m.; $|^2J(CC)| = 4.8$ Hz; $|^1J(CH)| = 122$ Hz; $^2J(SiCH) = +7.3$ Hz. [b] This value is for the unenriched isotopomer. The molecule $SiMe_3(^{13}CN)$ resonates 2 Hz (0.02 p.p.m.) to lower frequency. [c] Other parameters: δ(^{77}Se) = −346.41 p.p.m.; $|^1J(CSe)| = 275.0$ Hz; $|^2J(NSe)| = 3.66$ Hz. Longer-range couplings to Se were not detected. The parameters for this compound and $SiH_3(NCY)$ (Y = O or S) were measured at 233 K.

of cyanide groups. The n.m.r. parameters for this compound are collected in Table 1, and the ^{13}C-{^{1}H} spectrum (CN region) is illustrated in the Figure.

In a solution of the same compound in CH_2Cl_2 the coupling between the protons and the cyanide group collapsed after the solution had been allowed to stand at room temperature for an hour or so, implying that fast intermolecular exchange may be induced as a result of chemical reactions involving the solvent, or impurities, with $SiMe_3(CN)$; but in non-polar solvents there was no sign of the collapse of ^3J(CN) even after the solution had been kept at room temperature for extended periods.

Values of δ(^{15}N) and ^2J(SiN) were obtained from a sample of $SiMe_3(CN)$ containing 95% ^{15}N.

(*d*) *Carbon*-13 *Relaxation Studies of* $SiMe_3(CN)$.—The enriched $SiMe_3(^{13}CN)$ sample provided an opportunity to study relatively easily the relaxation of a non-protonated carbon. Measurements of T_1 and of the nuclear Overhauser enhancement (n.O.e.) were made at three temperatures, and the results are collected in Table 2.

TABLE 2

Relaxation parameters for the cyanide carbon of $SiMe_3(CN)$

θ_c/°C [a]	$T_1{}^t$/s [b]	η [c]	$T_1{}^{dd}$/s [d]	$T_1{}^0$/s [e]
12.5	100.6	0.40	500	126
25	97.1	0.31	622	115
37	93.1	0.25	740	106.5

[a] ±2 °C. [b] Total relaxation time ±10%. [c] Nuclear Overhauser enhancement ±0.1. [d] Carbon-13–hydrogen-1 dipole–dipole relaxation time, deduced from $T_1{}^t$ and η. [e] Relaxation time due to other mechanisms, deduced from $T_1{}^t$ and η.

DISCUSSION

The conclusions to be drawn from the observations reported here are clear. Any fast intermolecular exchange in systems like those studied here must presumably be derived from the presence of impurities; there is no evidence to support the proposal that any of the compounds we have studied exists in isomeric forms in solution in non-polar solvents. Moreover, the observed coupling constants make it quite clear that there is a direct bond between Si and C in both $SiH_3(CN)$ and $SiMe_3(CN)$, whereas Si is bonded to N in the other three compounds [the magnitude of ^2J(SiC) is known [7] to lie in the range 4—6 Hz]. There are of course limits on the levels at which we should expect to detect such impurities; it is always possible that weak peaks may escape detection either because of their weakness or because they lie under stronger resonances. However, we believe that we would have detected the presence of isomers of the kind postulated had they been present in concentrations greater than *ca.* 0.5%. From i.r. spectral studies, Booth and Frankiss [2] suggested that there might be 0.05% of $SiMe_3(NC)$ in the vapour of $SiMe_3(CN)$; our evidence does not allow us to comment on this view. On the other hand, our results are hard to reconcile with the report,[3] based on microwave spectroscopy, that the vapour of $SiMe_3(CN)$ contains up to 10% of $SiMe_3(NC)$. It is also worth noting that fast intermolecular exchange in these species may be very sensitive to the presence of impurities.

The n.m.r. parameters themselves are of some interest. In $SiH_3(NCY)$ the chemical shift of ^{15}N is remarkably sensitive to changes in Y, moving by 100 p.p.m. as Y changes from O to Se, but the shifts are very close to those reported for CH_3NCY (Y = O, −29 p.p.m.; Y = S, 47 p.p.m.).[8] The ^{1}H and ^{29}Si chemical shifts are characteristic of the atom bound to Si in the SiH_3 compounds, but ^2J(HN) in $SiH_3(NCY)$ is distinctly sensitive to Y. The values of $|^1J(SiC)|$ for the cyanides are somewhat less than one might have expected for an *sp* carbon;[9,10] presumably the electron-withdrawing properties of the nitrogen atom are responsible.

The absolute signs of the reduced coupling constants, K, where established by double-resonance experiments, are all positive; the signs of the coupling constants J thus depend only on the relative signs of the nuclear magnetic moments of the nuclei concerned.

Measurements of the nuclear Overhauser enhancement for the cyanide carbon of $SiMe_3(CN)$ shows that the dipolar relaxation time is exceedingly long at all three temperatures studied. This is not surprising for a quaternary carbon in such a small molecule with axial symmetry. The relaxation time due to other mechanisms decreases as the temperature increases, so it must be dominated by spin-rotation interactions. This result agrees with the conclusion of Lyerla *et al.*[11] that the shielding-anisotropy mechanism is not generally significant for ^{13}C at 2.35 T.

EXPERIMENTAL

Samples were prepared using standard vacuum apparatus, fitted either with greased glass or Sovirel polytetrafluoroethylene taps. Isotopically enriched K[CN] was converted into Ag[CN], which was treated with $SiMe_3I$ to give enriched $SiMe_3(CN)$ or with SiH_3Br to give $SiH_3(CN)$. Oxidation of aqueous K[CN] with $K[MnO_4]$ gave K[NCO]; refluxing K[CN] with sulphur in acetone gave K[NCS], and fusion of solid K[CN] with Se gave K[NCSe]. These salts were converted into the silver salts, which were then treated with SiH_3Br to give the silyl pseudohalides.

All samples were studied in 5-mm tubes; spectra of $SiH_3(CN)$ and $SiMe_3(CN)$ were run at ambient probe temperature, and spectra of $SiH_3(NCY)$, including ^{77}Se spectra, where the shifts were found to be sensitive to temperature changes, were recorded at low temperatures (233 K) to minimise sample decomposition. Most samples of SiH_3 derivatives were dissolved (3—5%) in CD_2Cl_2 containing a few percent of $SiMe_4$; the sample of $SiH_3(CN)$ in cyclopentane was 10% by volume. Samples of $SiMe_3(CN)$ were dissolved in benzene with C_6D_6 as a locking reference.

An XL100 spectrometer was used for the measurements of ^1H, ^{13}C, and ^{29}Si spectra of $SiMe_3(CN)$; this operates at 100.6 MHz for ^1H, 25.14 MHz for ^{13}C, and 19.87 MHz for ^{29}Si. Values of T_1 and η were measured as described in ref. 12; the use of benzene as solvent limited the temperature range over which relaxation times could be measured.

Other ^{29}Si and ^{13}C n.m.r. spectra, the ^{15}N spectrum of $SiMe_3(C^{15}N)$, and the ^{77}Se spectra were recorded on a Bruker WH 360 spectrometer, operating at 71.55 MHz for ^{29}Si, 68.68 MHz for ^{77}Se, 90.56 MHz for ^{13}C, and 36.50 MHz for ^{15}N. Double-resonance experiments, in which ^1H spectra of ^{28}Si or ^{29}Si species were observed whilst a single frequency in the ^{13}C or ^{15}N region of the spectrum was irradiated, were carried out using a Varian HA 100 continuous-wave spectrometer and a Schlumberger frequency synthesiser. Nitrogen-15 chemical shifts for the SiH_3 species were also obtained from these measurements.

Chemical shifts are reported using the ' high-frequency positive ' convention, relative to $SiMe_4$ for ^1H, ^{13}C, and ^{29}Si, $[NMe_4]I$ (which resonates at 10 133 352 Hz in a field such that the ^1H resonance of $SiMe_4$ is at 100.0 MHz) for ^{15}N, and $SeMe_2$ (20% in CH_2Cl_2) for Se.

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REFERENCES

[1] H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, 1968, **10**, 299.

[2] M. R. Booth and S. G. Frankiss, *Spectrochim. Acta, Part A*, 1970, **26**, 859.

[3] J. R. Durig, W. D. George, Y. S. Li, and R. O. Carter, *J. Mol. Struct.*, 1973, **16**, 47.

[4] D. Seyferth and N. Kahlen, *J. Am. Chem. Soc.*, 1960, **82**, 1080.

[5] J. E. Griffiths, *J. Chem. Phys.*, 1968, **48**, 278.

[6] J. R. Durig and J. F. Sullivan, *J. Mol. Struct.*, 1979, **56**, 41.

[7] R. K. Harris, J. D. Kennedy, and W. McFarlane, in ' NMR and the Periodic Table,' eds. R. K. Harris and B. E. Mann, Academic Press, New York, 1978, ch. 10.

[8] G. C. Levy and R. L. Lichter, ' Nitrogen-15 NMR Spectroscopy,' Wiley, New York, 1979, p. 72.

[9] G. C. Levy, D. M. White, and J. D. Cargioli, *J. Magn. Reson.*, 1972, **8**, 280.

[10] H. Dreeskamp and K. Hilderbrand, *Liebigs Ann. Chem.*, 1975, 712.

[11] J. R. Lyerla, D. M. Grant, and R. D. Bertrand, *J. Phys. Chem.*, 1971, **75**, 3967.

[12] R. K. Harris and B. J. Kimber, *J. Magn. Reson.*, 1975, **17**, 174.