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^{29}Si NMR STUDIES OF OLIGO- AND POLY-MERIC SILOXANES

III *. CYCLIC SILOXANES OF GENERAL FORMULA [MeRSiO]$_n$

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Summary

Silicon-29 NMR has been used, with proton noise decoupling, to study a number of cyclic siloxanes with asymmetric units. The chemical shifts observed are discussed in relation to the configurations of the various possible isomers. In the case of [MePhSiO]$_4$ the four possible isomers were examined separately; neighbour effects on chemical shifts are markedly non-additive, in contrast to the situation for the [MeHSiO]$_4$ isomers.

Introduction

Silicon-29 nuclear magnetic resonance spectroscopy is rapidly becoming a very important tool for structure determination in organosilicon chemistry, particularly in the study of silicones [3]. This situation has been made possible by the development of Fourier transform techniques, together with proton noise decoupling, better known for ^{13}C NMR. In the preceding paper of this series [2], we showed that the ^{29}Si chemical shifts of silicones containing the D′ unit, —$O_{1/2}Si(Me)(H)O_{1/2}$—, were influenced by the stereochemistry of neighbouring D′ units, i.e. tacticity effects were observable. The D′ group seems to be especially suitable for demonstrating these effects, since they have not been reported [4,5] for related chiral silicone groupings. As a consequence of this work, we felt it would be of interest to see whether ^{29}Si NMR could be used to differentiate between the various isomers of cyclic silicones containing the D′

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* Parts I and II are references 1 and 2 respectively.
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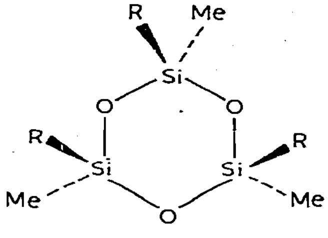
unit or related groups. We chose to examine a series of cyclic tetrasiloxanes of general formula $[MeRSiO]_4$ where R is hydrogen, phenyl (Ph) or vinyl (Vi). We have also examined some related cyclic siloxanes of formula $[MeRSiO]_n$, where $n = 3$ or 5. In the case of the two isomers of $[MePhSiO]_3$ and the four isomers of $[MePhSiO]_4$ we were able to examine the pure compounds, which had been separated previously [6], but in the other cases mixtures of isomers were studied.

For the trisiloxanes the possible isomers are I and II, whereas for the tetrasiloxanes the isomers III—VI may occur.



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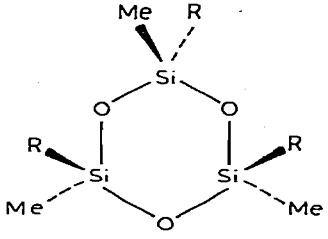

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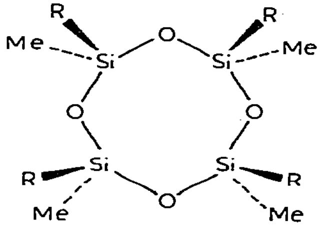

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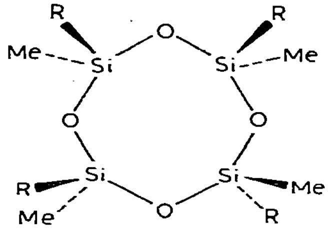

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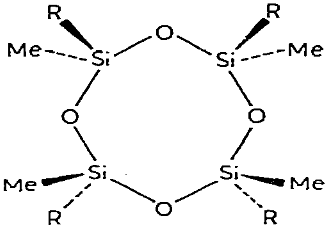

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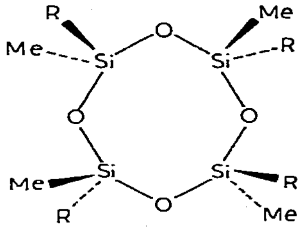

(VI)

For linear silicones containing the D′ unit only nearest-neighbour asymmetry effects on ^{29}Si chemical shifts were noticed [2], causing the resonance of a mid-chain D′ group to be split into a 1 : 2 : 1 triplet of average spacing ca. 0.8 Hz (the high-frequency spacing is smaller than the low-frequency spacing by ca. 0.4 Hz). For such compounds the asymmetry effects are presumably averaged over internal rotation, and it might be anticipated that larger variations are likely for cyclic molecules. If the tetrasiloxanes III to VI are considered it can be seen that there is a single ^{29}Si environment for each isomer except IV, which contains three different types of ^{29}Si. If a d*d*d or l*l*l triad arrangement is designated A, the d*d*l or d*l*l type of arrangement denoted B, and C refers to the d*l*d or l*d*l sequence, then the following environments are predicted: III — A, IV — A + 2B + C, V — 2B and VI — C. The relative coefficients given to these environments reflect the statistical probabilities of a given isomer and the equivalence of the silicon nuclei. Thus, for each of the isomers III, V and VI a single peak in the $^{29}Si—\{^1H\}$ spectrum is predicted, whereas for IV three peaks of relative intensity 1 : 2 : 1 are expected. If a statistically random mixture of isomers is in question, a 1 : 2 : 1 system of peaks due to environments A, B and C is also expected;

however, long-range effects from the fourth siloxy grouping will cause a further doublet splitting for each of these peaks since, for example, the A environments for I and IV are not identical. In general, such a splitting will presumably be appreciably smaller than the triplet average spacing. In an ideal situation, the influences of different orientations of neighbours would be additive, and a regular triplet of doublets would be seen. This is unlikely to be true in practice, so that the two triplet spacings are likely to be unequal (as observed [2] for the linear silicones containing the D′ group) as are the doublet spacings. Any such inequalities would undoubtedly be increased if there are differences in geometry between the isomers, as becomes likely if R is large. In such circumstances a random distribution of isomers may not be prepared, so that intensities can also vary from the ideal mentioned above.

Similar considerations can be applied to the analogous series of compounds $[MeRSiO]_n$ with $n \neq 4$. For $n = 3$, clearly I should give a single resonance of the type A, whereas II is expected to give two signals with intensity ratio 2 :1 of the B and C types, respectively. A statistically random mixture of I and II would thus give three signals with intensity ratio 1 : 2 : 1, and no further splittings would be expected. For $n = 5$ random mixtures of all isomers would again give three signals with intensities 1 : 2 : 1 in each case. Long-range effects would, of course, lead to additional fine structure. There are four isomers for $n = 5$, and it can be shown that these contain in total three types of A environment (one type being twice as probable as the other two) and, similarly, three types of C environment. There are four equally-probable B environments, two of which are rather similar (differing only in the sense that ll*d*dd differs from dl*d*dl). Thus for a random mixture of $n = 5$ isomers a maximum of 10 ^{29}Si—{^{1}H} peaks is expected. For an "ideal" situation these would simplify to a 1 : 2 : 1 triplet of 1 : 2 : 1 triplets; Additionally, as n increases from 4 the splittings due to asymmetry should decrease due to the extra flexibility of the ring systems. In the limit when n is very large, the influence of asymmetry should presumably approach the magnitude found [2] for linear systems.

Results and discussion

Figure 1 shows the ^{29}Si—{^{1}H} spectrum of a mixture of the cyclic compounds D'_4 and D'_5, as prepared. The signals at the left are due to D'_4, and the less intense lines on the right are due to D'_5. The frequencies of all the lines are given in Table 1. The shift difference between the arrowed peaks in Fig. 1 is 2.00 ppm, which is comparable to the shift difference for the corresponding cyclic compounds $[Me_2SiO]_4$ (δ(Si) —20.0 [8], —19.51 [9] ppm) and $[Me_2SiO]_5$ (δ(Si) —22.8 [8], —21.93 [9] ppm). The shifts for D'_4 are in reasonable agreement with the value (—33 ppm) reported by Holzman et al. [10] (no asymmetry effects were mentioned by these authors).

The D'_4 signals form an approximate 1 : 2 : 1 triplet, with a further doublet splitting for the central and high-frequency members. (It may be assumed that the lowest frequency triplet peak consists of an unresolved doublet.) This is the situation to be expected for a statistical distribution of isomers III—VI. The asymmetry effects are an order of magnitude greater than those found [2] for linear silicones containing the D′ group. The influences of the neighbours on the

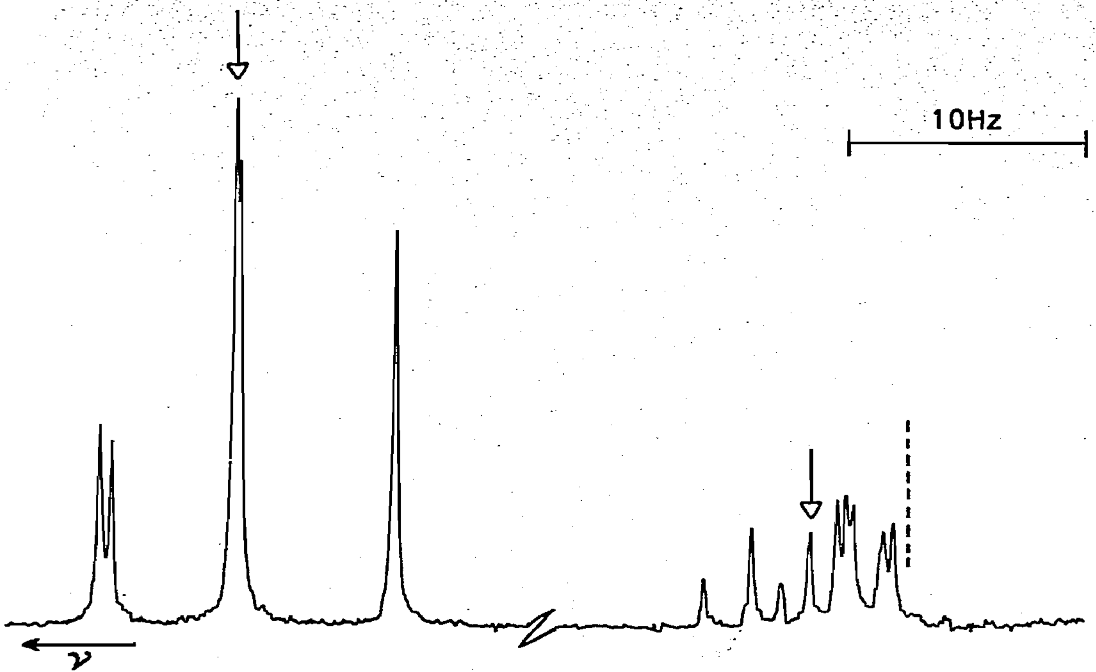

Fig. 1. 19.87 MHz ^{29}Si—{^{1}H} spectrum of a mixture of isomers of D'_4 and D'_5. The spectrum results from the accumulation of 504 transients with acquisition time 16.0 s and pulse width 50 μs. The arrowed peaks are referred to in the text. The vertical dashed line gives the reported position [2] of the central peak for mid-chain D′ groups of $MD'_{50}M$, where $M = Me_3SiO_{1/2}$.

shift of a given Si are not additive, but the discrepancies are not large. The long-range effect is an order of magnitude less than the shifts caused by nearest neighbours.

The D'_5 peaks are less easy to interpret. The total range is somewhat smaller than for D'_4, as expected because of the greater flexibility. Nine lines can be separately identified. Presumably there is a degeneracy for one of these, so that

TABLE I

^{29}Si CHEMICAL SHIFTS ^{a} FOR D'_4 and D'_5

D'_4		D'_5
δ(Si) (ppm)	Splitting (Hz)	δ(Si) (ppm)
−32.39	0.5	−34.45
−32.41		−34.55
−32.68	0.2	−34.61
−32.69		−34.68
−33.02		−34.73
		−34.75
		−34.77
		−34.83
		−34.85

^{a} Obtained indirectly (with respect to the signal of Me_4Si) as described previously [7].

TABLE 2

^{29}Si CHEMICAL SHIFTS FOR THE ISOMERS OF [MePhSiO]$_4$

Isomer	Environment	Ξ (Hz) [a]	δ(Si) (indirect) [b] (ppm)	δ(Si) (direct) [c] (ppm)
III	A	19 866 579.8	—30.41	—30.42
IV	B	19 866 583.4	—30.23	—30.25
	A or C	19 866 582.4	—30.28	—30.29
	C or A	19 866 581.9	—30.30	—30.33
V	B	19 866 585.6	—30.12	—30.11
VI	C	19 866 581.0	—30.35	—30.33

[a] Frequency for a field such that the protons in Me$_4$Si resonate exactly at 100 MHz [11]. [b] Obtained via Ξ as described previously [7]. [c] Obtained directly with respect to the ^{29}Si signal of internal Me$_4$Si.

the sample contains a complete mixture of isomers, as for D'$_4$. However, the spectrum cannot be readily assigned as a triplet with further fine structure, and it appears that long-range effects are relatively more important than is the case for D'$_4$. It is tempting to suggest that the three lines at highest frequency represent A (or C) environments, the next four are of B type, and the last two are C (or A) type with a degeneracy, but this is only one of several possible assignments, albeit the most likely. Definitive assignment would require separation of the isomers. The resonances for the central D' units of a long-chain linear polymer would also occur [2] in this region of the spectrum (see Fig. 1).

The availability of separate isomers of [MePhSiO]$_4$ has enabled a detailed investigation to be made. The number of ^{29}Si—{^{1}H} peaks observed in each instance is as expected, confirming the published structures, and the shift information is given in Table 2. The pattern of shifts is reproduced in Fig. 2. Two facts are immediately apparent:

(a) The total spread of frequencies is appreciably less than for [MeHSiO]$_4$, and it is clear that the D' unit is particularly good for showing nearest-neighbour asymmetry influences on chemical shifts. Presumably it would not be easy to resolve tacticity splittings for linear silicones containing the $-O_{1/2}Si(Me)(Ph)O_{1/2}-$ unit.

(b) The shift effects are not even remotely additive. There is, in fact, no discernible pattern to them. This is presumably an indication that steric or electronic influences distort the molecular structures. This reduces the value of the data as assignment aids, for example it does not allow the A-type and C-type peaks for D'$_4$ to be unambiguously distinguished.

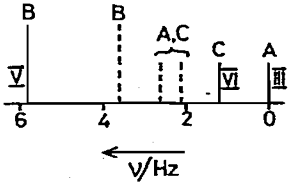

Fig. 2. Silicon-29 chemical shift pattern for the isomers of [MePhSiO]$_4$. The dashed lines refer to isomer IV. See the text for further explanation.

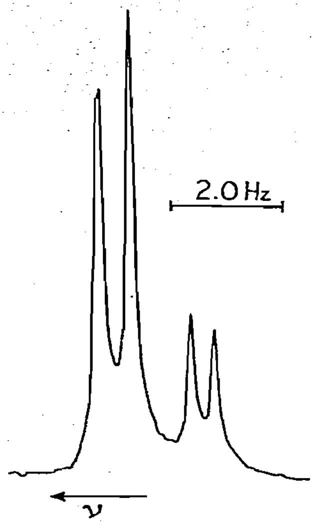

Fig. 3. 19.87 MHz ^{29}Si—{^{1}H} spectrum of a sample of [MeViSiO]$_4$ of unknown isomeric composition. The spectrum was obtained from the accumulation of 4223 transients.

Holzman et al. [10] have reported the shift of [MePhSiO]$_4$ (an unspecified isomer, or perhaps a mixture) as δ(Si) —32.0 ppm. This result is not in very good agreement with our data. The earlier authors did not mention any splitting of their peak.

The data for the [MePhSiO]$_4$ isomers was of some value in interpreting the ^{29}Si spectrum of a mixture of [MeViSiO]$_4$ isomers of unknown composition (Fig. 3), the chemical shifts for which are given in Table 3. Since four distinct peaks are seen, the sample must contain isomer IV plus at least one other isomer. In fact it is regarded as unlikely that the sample is other than a random mixture of isomers. This implies that there are several degeneracies in the spectrum. It is probable that each of the higher-frequency pair of peaks consists of two superimposed lines with intensity ratio 2 : 1, giving intensity ratios for the four observed peaks as 3 : 3 : 1 : 1.

The two isomers of [MePhSiO]$_3$ were also studied. In this case isomer II was studied first, giving two lines with a 2 : 1 intensity ratio. The more intense peak (environment) B is at Ξ = 19 866 773 Hz (δ(Si) —20.66 ppm), and the second

TABLE 3

^{29}Si CHEMICAL SHIFTS [a] FOR A SAMPLE OF [MeViSiO]$_4$

Ξ (Hz) [b]	δ(Si) (ppm) [c]	
19 866 535.4	—32.65	
19 866 534.9	—32.67	19 866 534.9
19 866 533.7	—32.73	
19 866 533.3	—32.75	

[a] See Fig. 3. [b] Frequency for a field such that the protons in Me$_4$Si resonate exactly at 100 MHz [11]. [c] Obtained directly via Ξ as described previously [7].

peak is 0.7 Hz to low frequency. Since the solution concentration for isomer II was unknown, isomer I was then added to the same NMR tube so that relative solvent effects were minimised. The peak due to I was found to be nearly superimposed on the weaker of the two peaks due to II. There was a small shift arising from concentration changes, the peak due to isomer I being at $\delta(\text{Si})$ −20.67 ppm, with those due to isomer II being 0.3 and 0.9 Hz to higher frequency. It will be noted that the shift effects due to nearest-neighbour configuration for $[\text{MePhSiO}]_3$ are smaller than those for $[\text{MePhSiO}]_4$. The C- and A-Type environments give signals to low frequency of the B environments for both $[\text{MePhSiO}]_3$ and $[\text{MePhSiO}]_4$. The isomers with $n = 3$ resonate to substantially higher frequency than those for $n = 4$, as is the case for $[\text{Me}_2\text{SiO}]_3$ ($\delta(\text{Si})$ −9.2 [8], −9.12 [9] ppm) and $[\text{Me}_2\text{SiO}]_4$ ($\delta(\text{Si})$ −20.0 [8], −19.51 [9] ppm).

A mixture of isomers of the cyclopentasiloxane $[\text{MePhSiO}]_5$ showed seven resolvable peaks of varying intensity in the ^{29}Si—$\{^1\text{H}\}$ spectrum between $\delta(\text{Si})$ −32.77 and −32.39 ppm. It did not prove possible to assign these signals. The total range (7.5 Hz) is comparable to that for $[\text{MeHSiO}]_5$ (8.0 Hz), in contrast to the corresponding cyclotetrasiloxanes.

The examples studied show that contraction of the ring from five to four siloxane units causes deshielding at ^{29}Si of between 1.8 and 2.8 ppm, which may be compared with the ca. 10 ppm deshielding caused by further ring-contraction to three siloxane units.

Experimental

The mixed sample of D'_4 and D'_5, and the sample of $[\text{MeViSiO}]_4$ came from the Silicones Operations Group, I.C.I. Ltd. (Organics Division). The isomeric $[\text{MePhSiO}]_n$ compounds were prepared by hydrolysis of MePhSiCl_2. Distillation under reduced pressure gave $[\text{MePhSiO}]_3$, $[\text{MePhSiO}]_4$ and $[\text{MePhSiO}]_5$ fractions as mixtures of stereoisomers. The individual isomers of $[\text{MePhSiO}]_3$ and $[\text{MePhSiO}]_4$ were separated as described previously [6]. For all the compounds C_6D_6 was added to provide a ^2H signal for field/frequency locking and referencing, and to provide a solvent. In the case of the isomers of $[\text{MePhSiO}]_4$ only, a consistent concentration was used, viz. 67.8% w/v in ca. 10% $\text{C}_6\text{D}_6/\text{C}_6\text{H}_6$, with tetramethylsilane added (to the extent of one-third of the volume of the solvent), after spectra had been recorded once, to serve as an internal reference for a second series of experiments. The samples were placed in 12 mm NMR tubes, which were not sealed.

The ^{29}Si—$\{^1\text{H}\}$ spectra were obtained at 19.87 MHz using a Varian XL 100 spectrometer as described previously [1,7]. In general the spectra were obtained using pulse widths of 15 μs (corresponding to a flip angle of ca. 10°), acquisition times of 8 s, spectral widths of 250 Hz, and ca. 200 transients were recorded. The experimental parameters for the spectra of D'_4 and D'_5 are, however, given in Fig. 1. In most cases the chemical shifts were calculated indirectly, as discussed in a previous publication [7]. All shifts $\delta(\text{Si})$ are quoted with respect to the ^{29}Si signal of Me_4Si, a positive number indicating that the sample resonates to high frequency of the reference.

The spectra were all arbitrarily phased to give positive intensities; the nuclear Overhauser enhancement factor was not measured.

Acknowledgements

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References

1 R.K. Harris and B.J. Kimber, J. Organometal. Chem., 70 (1974) 43.
2 R.K. Harris and B.J. Kimber, J. Chem. Soc. Chem. Commun., (1974) 559.
3 R.K. Harris and B.J. Kimber, Appl. Spect. Rev., 10 (1975) 117.
4 H.C. Marsmann, Chem. Z., 97 (1973) 128.
5 G. Englehardt, M. Mägi and E. Lippmaa, J. Organometal. Chem., 54 (1973) 115.
6 H.J. Hickton, A. Holt, J. Homer and A.W. Jarvie, J. Chem. Soc. C, (1966) 149.
7 R.K. Harris and B.J. Kimber, J. Magn. Res., 17 (1975) 174.
8 G. Englehardt, H. Jancke, M. Mägi, T. Pehk and E. Lippmaa, J. Organometal. Chem., 28 (1971) 293.
9 G.C. Levy and J.D. Cargioli, Proc. NATO Advanced Study Institute, Italy, 1972, in T. Axenrod and G.A. Webb (Eds.), NMR of Nuclei other than Protons, Wiley-Interscience, 1974, p. 251.
10 G.R. Holzman, P.C. Lauterbur, J.H. Anderson and W. Koth, J. Chem. Phys., 25 (1956) 172.
11 W. McFarlane, Proc. Roy. Soc. (London) A, 306 (1968) 185.