Journal of Organometallic Chemistry, 291 (1985) 153–157
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

IX *. THE EFFECT OF RING SIZE ON SILICON-29 NMR SHIFTS IN SILICON HETEROCYCLES

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(Received February 26th, 1985)

Summary

Silicon-29 NMR shifts for a series of 2,2-diphenyl-1,3,2-dioxasilacycloalkanes are reported and reveal a clear dependence of shift on ring size for rings of 5–14 atoms.

Over the last few years we have been interested in the synthesis and properties of 1,3,2-dioxasilaheterocycles and have already reported ^{29}Si NMR shifts for monomeric and dimeric organosilicon derivatives of 1,4-diols [2] and catechol [3]. From these and other shifts covering a wide range of compounds [4] it is now evident that, for this class of compound at least, an increase in ring size produces an upfield shift of the ^{29}Si NMR signal. Reports on this effect have been very limited, a fact which caused Marsmann to comment in his review of ^{29}Si NMR spectroscopy that "Except for siloxanes limited sets of ring sizes are available only" (1981) [5].

The ^{29}Si NMR shifts for a series of 2,2-diphenyl-1,3,2-dioxacycloalkanes, and their cyclic dimers, are given in Table 1 and shown plotted against ring size in Fig. 1 (mean values being used where isomers existed). The results are closely representative of those obtained from over fifty compounds [4] and serve to illustrate th following common characteristics:

1. Although some variation in shifts is apparent due to the steric effects of rin substituents in different isomers (< 3 ppm) there is an underlying, and mor substantial, dependences on ring size, with shifts of compounds in this pape spanning a range of 29 ppm (−7.5 to 36.5) for ring sizes from 5 to 14 atoms.
2. A striking feature is the large upfield shift which results from an increase in rin sizes 5 to 6 atoms (21.8 ppm) and which far exceeds the total subsequent increas from 6 to 14 atoms (7.2 ppm).
3. Shifts for larger ring sizes approach a limiting value which approximates to th

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* For part VIII see ref. 1.

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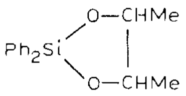
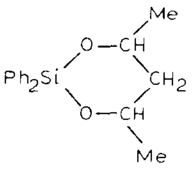
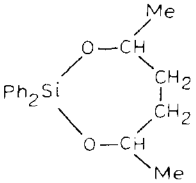
TABLE 1

^{29}Si NMR SHIFTS (ppm) (multiple values are due to isomers)

Compound	Monomer	Dimer
	−7.52	−31.48 −33.32 −33.94 −35.17 [a] −38.70 (mean −34.52)
	−28.25 −30.25 (mean −29.25)	−35.47
	−29.02 −30.25 (mean −29.64)	−35.17 −37.78 (mean −36.48)

[a] Major peak.

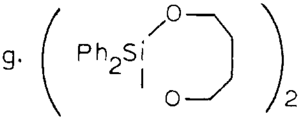
of the analogous acyclic dialkoxysilane, in this case taken to be diisopropoxysilane (−35.8 ppm; see Fig. 1) since both the alcohol and diol fragments contain oxygen bonded to secondary carbon atoms.

4. Significant dimerisation shifts occur for ring sizes of 5 to 7 atoms. In the present example they are:

Ring size	Dimerisation shift (ppm)
5 to 10	27.0
6 to 12	6.2
7 to 14	6.8

However our values for all 1,3,2-dioxasilacycloalkanes [4], irrespective of the nature of the substituents at silicon or carbon atoms, are almost all within 1 ppm of these values and hence dimerisation shifts may be of value in product identification. Similar shifts for dimerisation of the 5 membered (phenylenedioxy) silanes are somewhat larger at 36 ± 1 ppm and have previously been discussed [3].

We attribute each of the foregoing observations to the relief of ring strain in passing from smaller to larger rings and therefore conclude that bond angle strain is an important factor in determining ^{29}Si NMR shifts: an increase in ring strain leading to deshielding of the silicon nucleus. It follows that the largest rings, which can reasonably be assumed to be strain free, should give rise to shifts closely matching those of acyclic analogues. This is indeed found to be the case, as demonstrated by the example already cited and other results [4].

e.g.  , −32.25 ppm; $Ph_2Si(OEt)_2$, −32.36 ppm

It follows that 5-membered 1,3,2-dioxasilaheterocycles must be excessively strained and that this strain is largely relieved on passing to 6-membered, and higher, rings. Such a conclusion is consistent with chemical properties and known bond angle data. Hence it has been long known that derivatives of 1,2-diols are often difficult or impossible to obtain in the monomeric state and that these tend to polymerise on standing [6–8]. This is in contrast to the readily prepared 1,3-dioxolanes [6]. To our knowledge there are no bond angle data available for 1,3,2-dioxasilacycloalkanes as such but studies on acyclic compounds and related heterocycles suggest that Si–O–C bond angles should be large, and greater than 120°C, in strain-free structures (e.g. in $MeOSiH_3$, 121° [9]; α-naphthylphenylfluoromethoxysilane, 128° [10]; for a series of 2,2-dimethyl- and 2,2-diphenyl-1,3-dioxa-6-aza-2-silacyclooctanes, 126 to 133° [11]). Assuming other angles to be essentially tetrahedral (109°) the two Si–O–C angles would therefore need to be severely compressed in the 5-membered rings, in which the mean bond angles cannot exceed 108°. The same constraint does not apply to the 6-membered heterocycles where bond angles in the order of 120° are feasible.

Useful comparisons may be made with known data for silacycloalkanes and cyclosiloxanes (Table 2) and indicate a more general dependence of ^{29}Si NMR shifts

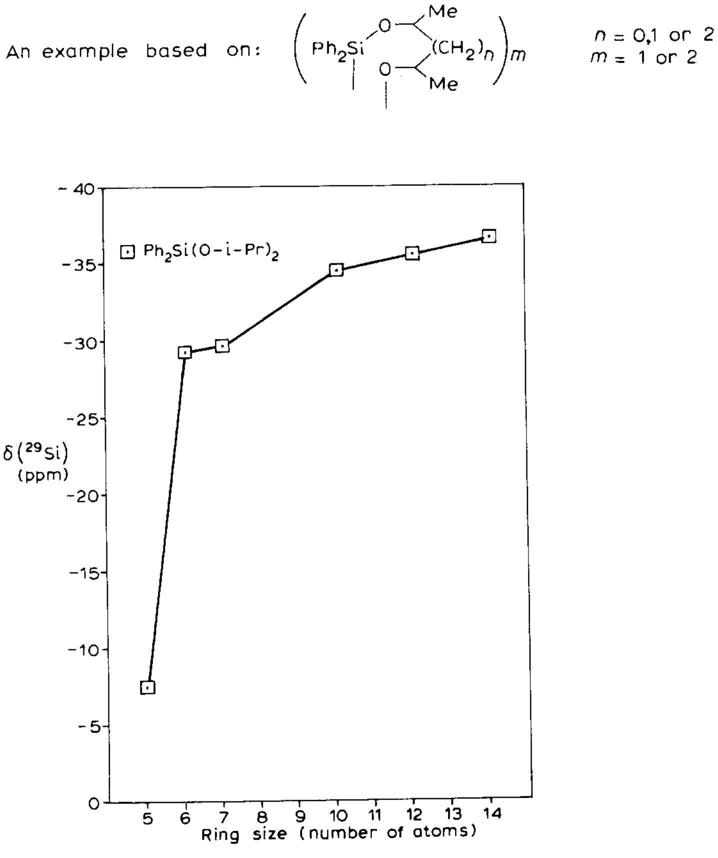
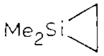
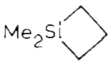
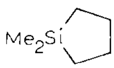
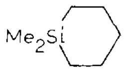


Fig. 1. Variation of $\delta(^{29}Si)$ with ring size.

TABLE 2

LITERATURE SHIFT DATA FOR SILAALKANES AND SILOXANES

Compound	$\delta(^{29}Si)$(ppm)	Ref.
Cyclic		
	−49.5	16
	+18.9	12
	+16.8	12
	−1.3	17
$(Me_2SiO)_3$	−9.2	14
$(Me_2SiO)_4$	−20.0	14
$(Me_2SiO)_5$	−22.8	14
$(Me_2SiO)_6$	−23.8	14
Acyclic		
Me_4Si	0	
Me_2SiEt_2	+5.0	12
$(Me_3SiOSiMe_2OSi^{\star}Me_2)_2O$	−23.4	5
Bulk D units in linear dimethylsiloxanes	− 22	18

on ring size. Scholl [12] noted that the silicon atom in silacyclopentane is deshielded by about 18 ppm compared to silacyclohexane. (The high-field shifts for silacyclopropanes are anomalous but, in any case, have no counterpart in the 1,3,2-dioxasilaheterocycles or cyclosiloxanes). Both Harris [13] and Engelhardt [14] commented on the low-field shift of silicon in the 6-membered hexamethyltrisiloxane (-9.2 ppm) compared with that in larger rings (-20 to -23 ppm) and linear polysiloxanes (~ -22 ppm). Lauterbur [15] noted the effect of strain on ^{29}Si NMR shifts in 1-oxa-2,5-disilacyclopentanes (e.g. 17 ppm lower field in the 2,2,5,5-tetramethyl compound that in hexamethyldisiloxane).

Comparing shifts for similar sized rings and acyclic compounds in each case the extent of deshielding is seen to be in the order, cyclosiloxanes > 1,3,2-dioxasilacycloalkanes > silacycloalkanes. Since Si–O–C bond angles are even greater than those already discussed for the Si–O–C fragment (eg. in $(H_3Si)_2O$, 144° [19]; $(Me_2SiO)_3$; 136° [20]; $(Me_2SiO)_4$, 142.5° [21]) it would appear that this deshielding is associated with the ring comparison in each heterocycle.

We conclude that there is likely to be a relationship between ^{29}Si NMR shifts and ring strain for silicon heterocycles in general.

Experimental

^{29}Si NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer in the FT mode. Samples used were as solutions in either $CDCl_3$ or CCl_4 with internal TMS as standard.

The compounds for the ^{29}Si NMR study were prepared by established methods [1,8], involving the interaction of a dichlorosilane and the corresponding diol in the presence of pyridine. Mass spectra and ^{29}Si NMR spectra were consistent with a predominantly monomeric nature of the products, although some additional peaks were present which were attributed to the dimer by analogy with other spectra.

Acknowledgement

We thank Dr. D. Smith for recording the NMR spectra.

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