

# Conformational Analysis of 2,5-Substituted 1,3-Dioxa-2-silacyclohexanes

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Results of the NMR analysis indicate that the free-energy difference between chair and boat conformations of the *cis*-2-*tert*-butyl-2,5-dimethyl-1,3-dioxa-2-silacyclohexane ring system is unusually low. The free energy difference between axial and equatorial substituents in position 5 of the 1,3-dioxa-2-silacyclohexanes is larger as compared to the pertinent cyclohexanes. Isomers with an axial substituent in the ring position 5 have not been detected.

Conformational studies on 1,3-dioxa-2-silacyclohexanes are scanty. Krieble and Buckhard<sup>1</sup> published the synthesis of 2,2-dimethyl-1,3-dioxa-2-silacyclohexane and later several substituted compounds have been prepared.<sup>2–9</sup> NMR studies on substituted 1,3-dioxa-2-silacyclohexanes have been reported twice.<sup>6,9</sup> Hellier<sup>8</sup> reported the NMR spectra of 2,2,5,5-tetra-substituted compounds, but only chemical shift data have been reported for the 5,5-dimethyl substituted compound.

This work was undertaken, partly because no relevant data on silicon analogues to 1,3-dioxanes or trimethylene sulfites were available in literature, and partly to obtain information on the conformational dependence of elongated bonds in cyclic sixmembered ring systems. Moreover, it was of interest to compare the effect of substituents in sixmembered ring systems containing silicon in the ring position 2, with analogous compounds containing sulphur or phosphorus. Only compounds with substituents in positions 2 and 5 have been studied by NMR.

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## EXPERIMENTAL

The 1,3-dioxa-2-silacyclohexanes were synthesized from the appropriate diols by the following procedures:

**Method A.** The 1,3-diol together with two mol of *N,N*-dimethyl amine were dissolved in a suitable solvent (ether, chloroform or benzene). An equimolar amount of the appropriate dichlorosilane was added dropwise and the mixture was refluxed for 4 h, filtered and the pure compound was obtained, after removal of solvent by distillation.

**Method B.** The 1,3-diol and a small amount of sodium methanolate were dissolved in benzene or mesitylene. The equivalent amount of the appropriate dimethoxysilane was added dropwise and the methanol formed was removed by azeotropic distillation with the solvent. The pure compound was obtained by distillation.

All non-commercial available 1,3-diols were synthesized from the appropriate malonates<sup>10</sup> by reduction with  $\text{LiAlH}_4$ .

*2,2-Dimethyl-1,3-dioxa-2-silacyclohexane (I).*<sup>7</sup> B.p.<sub>760</sub> 122 °C (b.p.<sub>23</sub> 35 °C),  $n_D^{20}$  1.4132, GC purity 99 %. Yield method A, 74 %, and method B, 85 %.

*2,2,5-Trimethyl-1,3-dioxa-2-silacyclohexane (II).* B.p.<sub>8</sub> 29 °C,  $n_D^{20}$  1.458, GC purity 98 %. Yield method A, 55 %, and method B, 72 %.

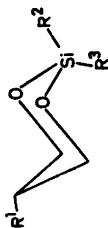
*5-tert-Butyl-2,2-dimethyl-1,3-dioxa-2-silacyclohexane (III).* Method A: B.p.<sub>8,5</sub> 69–71 °C,  $n_D^{20}$  1.4373, GC purity 98 %, yield 68 %. Method B: B.p.<sub>7</sub> 67–68 °C,  $n_D^{20}$  1.434, GC purity 98 %, yield 60 %.

*2-tert-Butyl-2-methyl-1,3-dioxa-2-silacyclohexane (IV).* B.p.<sub>30</sub> 38 °C, GC purity 98 %.

*2-tert-Butyl-2,5-dimethyl-1,3-dioxa-2-silacyclohexane [cis (V) and trans (VI)].* B.p.<sub>16</sub> 60–61 °C, azeotropic distillation with mesitylene. (The mesitylene was used as solvent during the preparation of the chlorosilane.)

GC specifications: The compounds were analysed and purified on a preparative gas chromatographic column, 2.1 m × 6 mm, containing either 15 % Apiezon L on Chromosorb W HMDS

Table 1. Coupling constants (Hz) and chemical shifts (ppm from TMS) at 27 °C.



Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	<sup>2</sup> J <sub>4(o)</sub>	<sup>2</sup> J <sub>6</sub>	<sup>3</sup> J <sub>4aaa</sub>	<sup>3</sup> J <sub>4esa</sub>	<sup>4</sup> J <sub>4aaa</sub>	<sup>4</sup> J <sub>4aac</sub>	<sup>4</sup> J <sub>4esc</sub>	<sup>3</sup> J <sub>CH<sub>3</sub>H</sub>	<sup>3</sup> J <sub>4a(aa)</sub>	<sup>3</sup> J <sub>4c(ec)</sub>	<sup>1</sup> ν <sub>sa</sub>	<sup>1</sup> ν <sub>R<sup>1</sup></sub>	<sup>1</sup> ν <sub>R<sup>2</sup></sub>	<sup>1</sup> ν <sub>R<sup>3</sup></sub>	RMS
I	H	CH <sub>3</sub>	CH <sub>3</sub>	<sup>a</sup>	<sup>a</sup>	7.10	3.46	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	3.93	3.93	3.93	1.72	1.72 <sup>b</sup>	0.8	0.08	0.10
II	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	-10.89	9.49	9.49	3.97	0.47	-0.45	1.85	6.85	3.57	3.88	0.70	0.70	0.05	0.05	0.06
II <sup>b</sup>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	-10.96	9.39	9.39	3.97	0.25	-0.31	1.78	6.82	3.56	3.89	0.69	0.69	0.05	0.06	0.05
III	<i>t</i> -Bu	CH <sub>3</sub>	CH <sub>3</sub>	-11.06	10.55	10.55	4.06	-0.27	-0.59	1.88	3.80	4.05	4.05	1.74	0.82	0.08	0.08	0.12
IV	H	<i>t</i> -Bu	CH <sub>3</sub>	<sup>a</sup>	-13.0	4.25	6.50	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	3.93	3.93	3.93	1.63	1.75 <sup>c</sup>	0.08	0.97	<sup>d</sup>
V	CH <sub>3</sub>	<i>t</i> -Bu	CH <sub>3</sub>	-11.0	9.5	4.0	4.0	-0.1	-0.3	1.9	6.9	3.59	3.93	0.67	0.67	0.08	0.95	<sup>d</sup>
VI	CH <sub>3</sub>	CH <sub>3</sub>	<i>t</i> -Bu	-11.0	10.5	4.0	4.0	-0.1	-0.3	1.9	6.9	3.51	3.87	0.57	0.57	0.95	0.08	<sup>d</sup>

<sup>a</sup> Parameters cannot be calculated from spectra. <sup>b</sup> Temperature 58 °C. <sup>c</sup> R<sup>1</sup>=H. <sup>d</sup> Non-iterative calculations (see the text); errors in the coupling constants are ca. 0.3 Hz.

or 10 % Apiezon L on Fluoropak HMDS.

**NMR specifications:** The materials were introduced into 5 mm o.d. NMR sample tubes, directly from the gaschromatograph. A suitable solvent as well as a small amount of TMS were added to serve as locking and reference substance. The samples were degassed by the freeze-pump-thaw technique. The spectra were recorded on a 60 MHz JEOL-C-60-H instrument. All spectra were recorded in internal lock mode with frequency sweep at *ca.* 50 Hz sweep width and calibrated every 5 Hz using a frequency counter. The counter was accurate to 0.1 Hz and the line positions were taken as the average of several spectra. The computations were carried out on an IBM 360/50 computer and the graphical output was obtained using a Calcomp plotter.

### SPECTRAL ANALYSIS

The spectrum of 2,2-dimethyl-1,3-dioxa-2-silacyclohexane (I) can be divided into three regions; a triplet at  $\delta$  3.9, a multiplet at  $\delta$  1.7, and a singlet at  $\delta$  0.1. The triplet at high frequency is assigned to the protons in positions 4 and 6, and the multiplet to protons at carbon 5. The singlet is due to the methyl groups attached to the silicon. The spectrum was analysed as an  $[ABC]_2$  spin-system (Table 1). The RMS value obtained was 0.1 when 67 theoretical lines were correlated to observed transitions and 14 parameters were allowed to vary.

The spectrum of 2,2,5-trimethyl-1,3-dioxa-2-silacyclohexane (II) contained four bands at  $\delta$  0.05,  $\delta$  0.7,  $\delta$  2.0, and  $\delta$  4.0–3.7. The two low frequency bands are assigned to the methyl groups. The high frequency band is assigned to protons at carbon 4 and 6 and the band at  $\delta$  2.0 to the protons in the ring position 5. The spectrum was analysed as an  $[AB]_2CD_3$  spin-system. Spectra obtained at 27 °C and 50 °C were analysed (Table 1). The RMS value obtained in both cases was 0.06 when 18 parameters were allowed to vary and 185 lines were correlated to observed transitions.

The spectrum of 5-*tert*-butyl-2,2-dimethyl-1,3-dioxa-2-silacyclohexane (III) consists of four bands at  $\delta$  0.08,  $\delta$  0.82,  $\delta$  1.74, and  $\delta$  4.1–3.7. The two low frequency bands are due to the two methyl groups and the *tert*-butyl group. The bands at  $\delta$  4.1–3.7 and  $\delta$  1.7, assigned to protons at  $C_4(C_6)$  and  $C_5$  (Fig. 1), respectively, were analysed as an  $[AB]_2C$  spin system. The

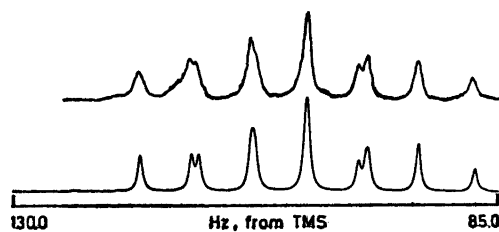


Fig. 1. The observed spectrum (upper) and the calculated spectrum of proton 5 of 5-*tert*-butyl-2,2-dimethyl-1,3-dioxa-2-silacyclohexane (III).

RMS value obtained was 0.12 when 40 theoretical lines were correlated to observed transitions and 15 parameters were allowed to vary.

The NMR spectrum of 2-*tert*-butyl-2-methyl-1,3-dioxa-2-silacyclohexane (IV) appeared to be deceptively simple, with a triplet at  $\delta$  3.93, a complex band at  $\delta$  1.63 and singlets at  $\delta$  0.97 and  $\delta$  0.08 integrating to 4:2:9:3, respectively. The spectrum could be reproduced by assuming an  $[A]_4CD$  spin system, but iterative calculations were not feasible, as the experimental spectrum had too little fine structure. Parameters used in the non-iterative calculation are listed in Table 1. The errors in the parameters are *ca.* 0.3 Hz. The GC analysis of 2-*tert*-butyl-2,5-dimethyl-1,3-dioxa-2-silacyclohexane (V and VI) dissolved in mesitylene showed only one peak for this compound. The NMR spectrum, however, gave a complex pattern with singlets at  $\delta$  0.95 and  $\delta$  0.08, two doublets at  $\delta$  0.67 and  $\delta$  0.57, a broad unresolved band centered at *ca.*  $\delta$  2.0, and a region at  $\delta$  4.0–3.4 containing eleven complex peaks (Fig. 2). The signals at  $\delta$  4.0–3.4, assigned to the protons at carbons 4 and 6, were analysed as two overlapping  $[AB]_2$  parts of  $[AB]_2CD_3$  spin systems. Only non-iterative calculations were performed. The calculated spectrum of parameters of Table 1 is shown in Fig. 2. The errors in the coupling constants are *ca.* 0.3 Hz.

### RESULTS AND DISCUSSIONS

*2,2-Dimethyl-1,3-dioxa-2-silacyclohexane (I).* The observed chemical shifts (Table 1) are close to those reported by Hellier<sup>8</sup> and Voronkov *et al.*<sup>4</sup> The reported<sup>8</sup> vicinal coupling constant 5.4 Hz is, however, the mean value

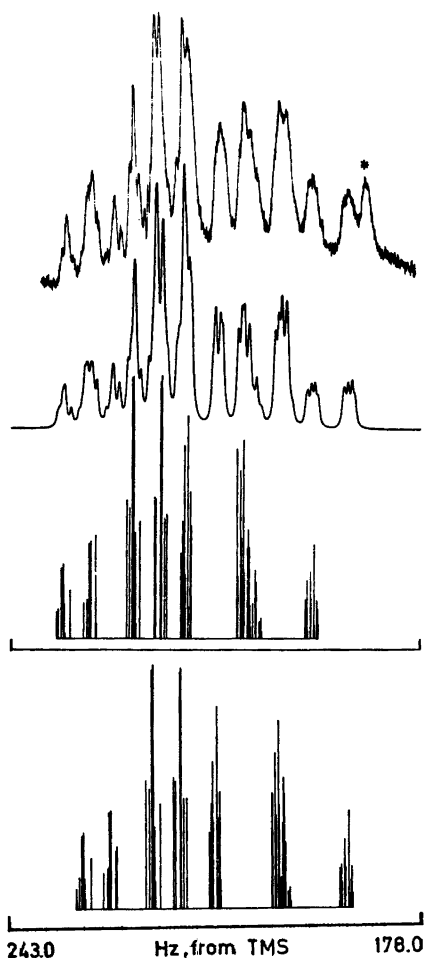


Fig. 2. The observed spectrum (upper) of protons at carbons 4 and 6 of *cis*- and *trans*-2-*tert*-butyl-2,5-dimethyl-1,3-dioxane-2-silacyclohexane (V and VI). The theoretical spectrum is shown below. The stickplots show the individual spectra of the *cis*- (upper) and *trans*- (lower) isomer (see the text). \* = impurity.

of the coupling constant obtained by us, 7.09 Hz and 3.46 Hz (Table 1). The chemical shift data and the lack of any observable geminal coupling constants suggest a rapid equilibrium between two equivalent chair conformations. The 1,3-dioxane has been reported<sup>11,12</sup> to exist in a 1:1 equilibrium between two chair conformations. The observed vicinal couplings of compound I are of the same magnitude as observed in dioxanes. Moreover, considering the sym-

metry of I, it is reasonable to assume a 1:1 equilibrium between two chair conformations for compound I too. The NMR spectrum of compound I in CS<sub>2</sub> was examined in the temperature range +27 °C to -88 °C,\* but the coalescence temperature was not reached and no noticeable changes of the spectra were observed. A coalescence temperature below -88 °C indicates a lower inversion barrier as compared to 1,3-dioxane. This is a reasonable assumption because coupling constants and chemical shift differences of the siloxanes examined (Table 1) are close to pertinent values obtained for dioxanes.<sup>18</sup> Regardless of the transition states, inversion between chairforms involves rotations about single bonds. To the authors knowledge, no values of the rotation barrier about Si-O bonds have been reported. The Si-O bond length, 1.63 Å,<sup>14</sup> as compared to C-O, 1.43 Å, causes a "flattening" of O-Si-O ring moiety as compared to the O-C-O part of the dioxane ring. The effect of longer bonds on the rotation barrier can be seen from CH<sub>3</sub>-SiH<sub>3</sub>, where the barrier is estimated to *ca.* 1.9 kcal/mol<sup>14</sup> as compared to the ethane barrier of *ca.* 3.0 kcal/mol. Introduction of a single bond, into a cyclic system, with lower rotation barrier should lower the inversion barrier of the ring-system. Geminal methyl groups at carbon 2 in dioxane lowers the barrier from 9 kcal/mol to about 7.8 kcal/mol,<sup>15</sup> and the methyl groups attached to the silicon atom might cause a similar lowering of the barrier in compound I.

Assuming an equilibrium between two equally populated chair forms, the two observed vicinal coupling constants can be expressed by  $^3J_{\text{obs}} = \frac{1}{2}(J_{\text{aa}} + J_{\text{ee}})$  and  $^3J_{\text{obs}} = \frac{1}{2}(J_{\text{ae}} + J_{\text{ea}})$ . This enables us to calculate dihedral angles for the chair conformation by the *R*-value method,<sup>16</sup> giving *R* = 2.05, corresponding to a dihedral angle about 57° of the -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-moiety. The *R*-value is essentially the same as those obtained from NMR measurements on various six-membered ring compounds,<sup>16-18</sup> which are shown to exist in chair conformations.

*2,2,5-Trimethyl-1,3-dioxane-2-silacyclohexane* (II). The NMR data obtained for this compound clearly indicates that it exists in a chair

\* The temperature ranges for compounds I and II (*vide infra*) are decided from solubility restrictions.

conformation or an equilibrium between two chair forms. The silicon methyl groups appear to be a broad but split signal, indicating two different methyl groups. The couplings 9.5 Hz and 3.97 Hz (Table 1), assigned to  ${}^3J_{4a5a}$  and  ${}^3J_{4esa}$ , indicate that the methyl group at carbon 5 is predominantly in the equatorial position. The coupling constants suggest that compound II exists almost entirely in a conformation with an equatorial methyl group at carbon 5. The NMR data obtained at 58 °C are not sufficiently different from those obtained at 27 °C, to make any calculations of conformational energies feasible. There was, however, no significant changes in the spectrum between -70 and +58 °C. The latter observation might indicate a chair-twist rather than a chair-chair equilibrium where an equatorial methyl group at carbon atom 5 is expected to be at least 0.8 kcal/mol<sup>19</sup> more stable as compared to the axial position. The large value of  ${}^4J_{ee}$ , 1.85 Hz, suggests a chair-twist equilibrium or that II exists in a rigid chair form.

*5-tert-Butyl-2,2-dimethyl-1,3-dioxa-2-silacyclohexane (III)*. The coupling constants obtained are close to values of compound II, except for  ${}^3J_{aa}$ , which is substantially larger, 10.6 Hz. The coupling constants (Table 1) indicate that compound III exists predominantly in a chair conformation with the tertiary butyl group in the equatorial position. No significant changes of the spectrum was observed between -107 and +197 °C, and it is therefore reasonable to assume that III constitutes an anancomeric system.

*2-tert-Butyl-2-methyl-1,3-dioxa-2-silacyclohexane (IV)*. The spectrum of compound IV appeared to be deceptively simple. The protons at C<sub>5</sub> are, however, not equivalent with chemical shift difference about 0.1 ppm. The coupling constants obtained, 6.5 Hz and 4.3 Hz, are substantially different from the values of I and this suggests an equilibrium different from that assumed for compound I. An equilibrium between two twist conformations can explain a chemical equivalence of protons at carbons 4 and 6 and a non-equivalence of protons at carbon 5. An estimate of the vicinal coupling constants of an equally populated twist-twist equilibrium, *ca.* 6.5 Hz and *ca.* 4.3 Hz, can be calculated from coupling values suggested by Wücherpfennig.<sup>20</sup> Recently Pihlaja *et al.*<sup>21</sup> re-

ported the existence of twist forms in 1,3-dioxanes. The longer Si-O bond as compared to the C-O bond could reduce the equatorial preference of a 2-*tert*-butyl group, but it might also make twist conformations more probable.

*cis- and trans-2-tert-Butyl-2,5-dimethyl-1,3-dioxa-2-silacyclohexane (V and VI)*. The NMR spectrum of this sample clearly indicated, in spite the appearance of only one peak in GC, the existence of more than one compound. The complexity of the spectrum made it feasible only to analyse the region  $\delta$  3.4-4.0 (Fig. 2), assigned to protons in ring-positions 4 and 6. The region assigned to the proton at C<sub>5</sub> did not show any resolved fine-structure, and hence it was not possible to obtain any information from this band.

The band at  $\delta \sim 3.5$  can only be reproduced upon the following assumptions (see Fig. 2): (a) The spectrum consists of two superimposed spectra due to closely related spin-systems and (b) The methyl group at carbon 5 occupies the equatorial position in both compounds. The two superimposed spectra are both of the [AB]<sub>2</sub>CD<sub>2</sub> type. From the magnitude of relevant coupling constants and chemical shifts (Table 1) and the symmetry of the spin system, it is reasonable to assume that both isomers exist in a chair conformation. Entry VI is tentatively assigned to the *trans* isomer with the methyl group at carbon 5 and the *tert*-butyl group in the equatorial position. The existence of a large coupling constant in both isomers indicates equatorial methyl groups. This implies that the *tert*-butyl group in the *cis* isomer V is situated axial or V exists in a boat conformation or in a chair-boat equilibrium. The Si-O bond (1.63 Å) is considerably longer compared to the C-O (1.43 Å) and the P-O bond (1.54 Å). The equatorial preference of a *tert*-butyl group on silicon might be less as compared to pertinent carbon and phosphorus analogues. The large coupling  ${}^3J_{aa}$  excludes any equilibrium between twist conformations.

Boat forms of six-membered saturated ring compounds are normally 5-6 kcal/mol higher in free energy ( $\Delta G^\circ_{25}$ ) than the corresponding chair conformations.  $\Delta H^\circ$  (chair-boat) for cyclohexane and 1,3-dioxane are roughly those estimated from the rotational barriers in propane<sup>27</sup> and dimethyl ether.<sup>28</sup> It is expected that for other heterocycles the  $\Delta G^\circ_{25}$  (chair-

boat) may be less than 6 kcal/mol depending primarily on rotational barriers, as yet unknown. It is assumed that the rotational barrier of  $\text{CH}_3-\text{CH}_2-\text{Si}-\text{CH}_3$ <sup>24</sup> is less than the value of the carbon analogue. The longer Si-X bond as compared to the C-X bond may be the reason for this. A lower rotational barrier about the Si-X bond,<sup>24</sup> as compared to the C-X bond, together with a more favourable equatorial *tert*-butyl group suggest the existence of a boat conformation or a chair-boat equilibrium for compound V. The existence of a boat conformation for *cis*-2,5-di-*tert*-butyl-1,3,2-dioxaphosphorinan-2-one<sup>25</sup> is shown, based on the magnitude of the coupling between the phosphorus atom and the protons at carbons 4 and 6. Certain 1,3-dioxanes, substituted at carbons 2 and 5, have been reported to exist in boat conformations.<sup>26-29</sup>

## CONCLUSION

The barrier to ring inversion in siloxanes is probably less than the barrier observed for analogous 1,3-dioxanes. Twist and boat conformations must be considered when discussing conformational equilibria of 1,3-siloxanes. Contribution from non-chair forms is assumed to be due to a lower rotational barrier together with a substantial longer Si-X bond as compared to carbon analogues. There is no evidence for the existence of isomers with an axial substituent at carbon 5. The free energy difference between axial and equatorial substituents in position 5 is apparently larger for 1,3-siloxanes as compared to cyclohexanes and 1,3-dioxanes.

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