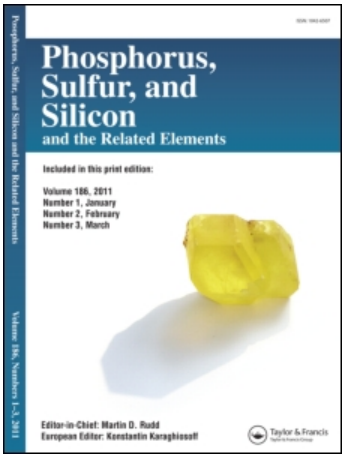

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A New Class of Silatranes[1]

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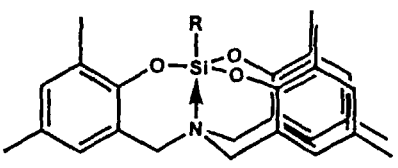
A series of silatranes containing all six-membered rings $N[CH_2(Me_2C_6H_2)O]_3SiR$ was prepared using tris(2-hydroxy-4,6-dimethylbenzyl)amine as the encapsulating agent. VT ^1H NMR spectra reflected fluxional behavior for all of these chiral molecules. The activation energies for enantiomeric conversion of the propeller-like silatranes correlated with the extent of structural rigidity associated with the ring system. The degree of nitrogen donor interaction depends primarily on electronegativity effects induced at silicon by the exocyclic ligand.

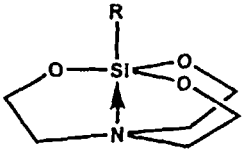
Keywords: silatranes; six-membered rings; nitrogen donor action; fluxionality; enantiomeric conversion

INTRODUCTION

We recently prepared a new class of silatranes (**A-D**) containing all six-membered rings[2] which contrasts with previous work that centered on related silatranes (**E-H**) containing five-membered rings.[3-6] It was shown that the silatrane systems with the larger rings allowed substituent



	R
A	Me
B	OMe
C	Ph
D	CCl_3

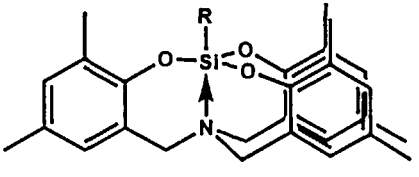


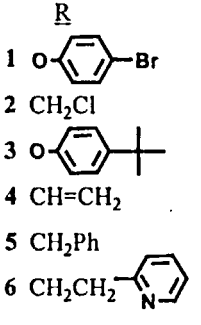
	R
E^3	Me
F^4	OEt
G^5	Ph
H^6	Cl

effects associated with the axial position of the resulting trigonal bipyramidal structures (TBP) to be reflected in dramatically altering the Si-N bond interactions as well as in changes of the ^{29}Si chemical shifts.[2] For example, changing the axial group from methyl in silane **A** to phenyl in silane **C** resulted in a change in the Si-N distance from 2.745(4) Å to 2.238(3) Å (ave.) for these silatranes composed of all six-membered rings.[2] A corresponding substitution in the five-membered ring silatranes **E**[3] and **G**[5] produced a Si-N distance alteration which did not significantly change, i.e. 2.175(4) Å for the methyl substituted silatrane **E** and 2.160(4) Å (ave.) for the phenyl substituted silatrane **G**.

On comparison of the series of newly formed silatranes having the six-membered rings[2], X-ray analysis showed a variation of over 0.7 Å in the Si-N distance while the analogous series with five-membered rings[3-6] ranged only over 0.15 Å. It was concluded[2] that the greater rigidity imposed by the presence of five-membered rings in all previously studied silatranes[7-9] limited the extent of Si-N interaction that could be studied by substituent variations.

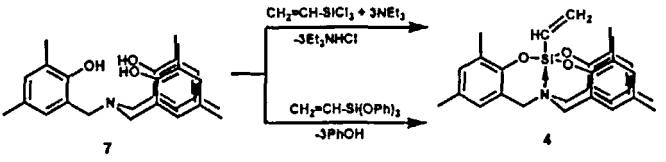
We now have synthesized a more extensive series of silatranes containing six-membered rings which encompasses a wider variation in ligand substitution. Both tetraoxy silanes (**1** and **3**) and monoorganotrioxy silanes (**2** and **4-6**) are included in this study.





SYNTHESES

The silatranes **1-6** were synthesized using three different methods. Silatranes **2, 4B** and **5** were synthesized by the reaction of the triphenol **7** with an appropriate trichlorosilane in the presence of triethylamine. The silatranes **4A** and **6** were obtained by transesterification of triphenoxyvinylsilane and trimethoxy-2-(2-pyridyl)ethylsilane, respectively, with the triphenol **7**, whereas silatranes **1** and **3** were obtained by the transesterification of the preformed silatrane **B** with the appropriate phenol through the replacement of the methoxy group. The methods are illustrated in equations 1-2 for the formation of **4B** and **4A**, respectively. All of the new silatranes **1-6** incorporate the triphenol **7** as the encapsulating agent.



(1)

(2)

STRUCTURE

X-ray analysis shows that all ten silatranes have structures that are pentacoordinate and vary in their degree of trigonal bipyramidal character (TBP) due to the extent of Si-N coordination. A representative ORTEX plot is shown in Figure 1 for **3**. The displacement from a tetrahedral geometry toward a TBP can be judged from the Si-N distances summarized in Table 1. The % TBP displacement is shown in the next to the last column. The degree of silatrane TBP character is estimated from the approach of the Si-N distance to the sum of the silicon and nitrogen covalent radii of 1.93 Å relative to that for the sum of the van der Waals radii of 3.65 Å. It is seen that as the Si-N distance decreases from 2.838(4) Å to 2.025(4) Å, the displacement from a tetrahedron toward a TBP increases from 47% to 95%.

The type of correlation discussed above with reference to Table 1 does not exist for previously studied silatranes[3-9], all of which contain five-membered rings[3-6]. Due to ring constraints in over 60 of these systems, the Si-N distances found in the crystalline state are confined to a narrow range, 1.965(5)-2.240(9) Å.[7-9]

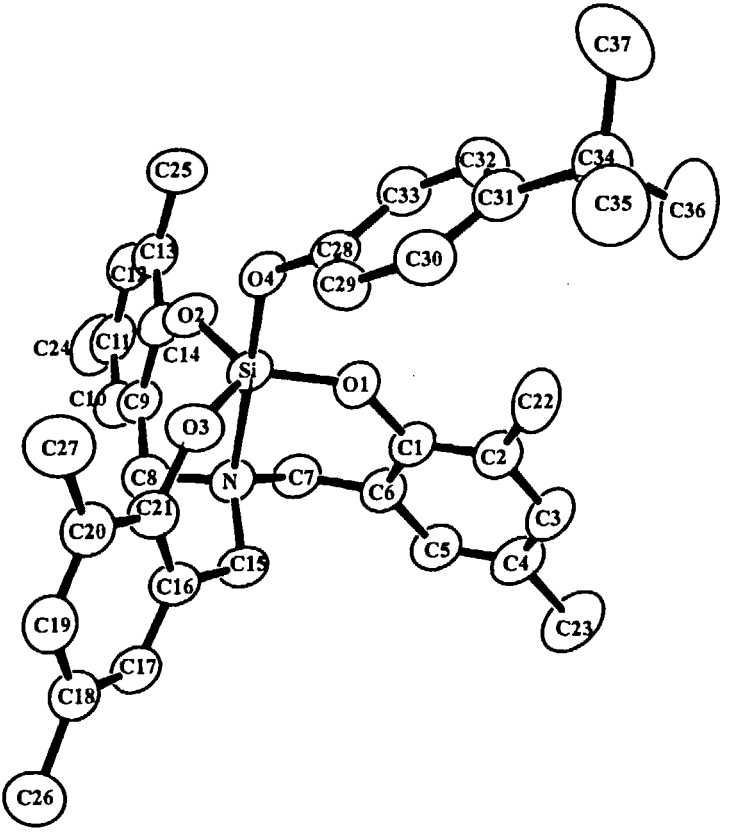


FIGURE 1. ORTEX diagram of **3**

TABLE 1. Comparison of Si-N Distances and ^{29}Si Chemical Shifts for Silatranes that have Six-Membered Rings.

Compound	Group R	Si-N Å	$\delta(^{29}Si)^b$, ppm	%TBP	$\Delta G^{\ddagger}$ kcal/mole
D[a]	CCl_3	2.025(4)	-140.8	95	>16.6
1[c]	OC_6H_4-4-Br	2.11(1)	-142.5	90	11.5
2	CH_2Cl	2.112(4) 2.130(5)	-123.8	89 88	11.8
3[c]	OC_6H_4-4-Bu-*t*	2.166(3)	-136.0	86	11.2
C[a]	Ph	2.193(3) 2.283(3)	-110.7	82 82	9.7
4A	$CH{=}CH_2$	2.542(4)	-97.2	64	10.1
4B	$CH{=}CH_2$	2.636(4)	-97.2	59	
5	CH_2Ph	2.563(5)	-101.3	63	9.3
B[a,c]	OMe	2.633(6)	-119.0	59	10.4
A[a]	Me	2.745(5)	-74.5	53	10.3
6	CH_2CH_2-2-C_6H_4N	2.781(4) 2.838(4)	-91.3	51 47	9.1

a Reference 2. b In CH_2Cl_2. c These three are tetraoxysilanes while the others are monoorganotrioxysilanes.

NMR SPECTROSCOPY

Figure 2 displays a plot of the variation in ^{29}Si chemical shift with the Si-N donor distance for the silanes listed in Table 1. Silatranes **1**, **3**, and **B**

form a series of tetraoxysilanes which differ relative to their ^{29}Si shift (lower line) compared to the monoorganotrioxysilanes (upper line). For both classes, as expected, there is a general upfield shift in the ^{29}Si value with increasing nitrogen donor coordination.

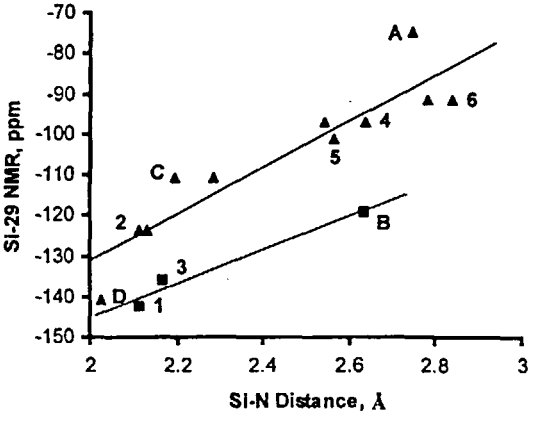


FIGURE 2. ^{29}Si chemical shift *vs* the Si-N distance for tertraoxysilatranes (■) and for monoorganotrioxysilatranes (▲).

Although not perfect, the order of points for the trioxysilanes in Figure 2 corresponds to electronegativity effects induced at silicon by most of the axial substituents. Similarly, the order of increasing electronegativity of the axial groups is expressed at silicon for the tetraoxysilanes: **1>3>B**. Here, replacement of the electron withdrawing *p*-bromo group in **1** with an electron donating *p*-*t*-butyl group to give **3** results in a decrease in the nitrogen donor interaction while a change to

an axial OMe groups causes a much more substantial decrease in this interaction along with a downfield shift in the ^{29}Si value.

A variable temperature NMR study of the NCH_2 proton signals, eg. for **2** and **4A**, shows spectra at low temperature (~185 K) that comprise two doublets of equal intensity. On warming to 290 K, only a singlet is present. Thus, the signals of each of the methylene protons, which are different at low temperature and couple with each other, coalesce and time average. The process that makes the methylene protons become equivalent is most likely associated with the presence of a racemic mixture of the chiral silatranes which are rapidly intraconverting at room temperature. This applies to all of the silatranes in Table 1 other than that for **D** which is a rigid entity.[2] As shown in Figure 3 for **2**, the three rings most likely flip or pseudorotate simultaneously to cause the

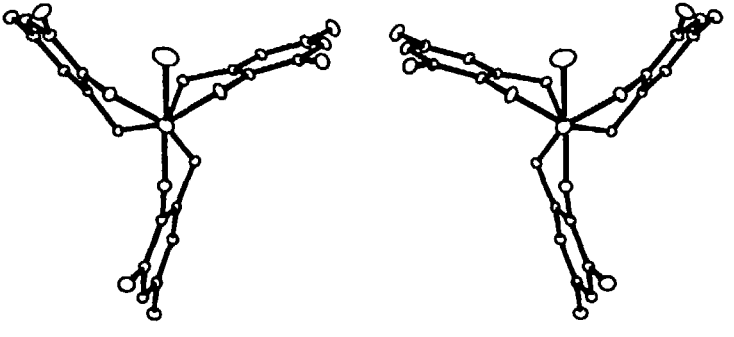


FIGURE 3. ORTEX diagram showing the propeller arrangements of the clockwise and anti-clockwise orientations of the centrosymmetric related molecules of **2**. Both are viewed along the CH_2-Si-N axis with CH_2Cl at the top.

clockwise and counterclockwise propeller orientations to interchange with one another. The activation energies $\Delta G^{\ddagger}$ are listed in Table 1. There is a noticeable increase in $\Delta G^{\ddagger}$ of over 2.5 kcal/mol from **6** to **1** as the degree of nitrogen donor action increases measured by the decrease in Si-N distance. Since **D**, with the most electronegative axial group (CCl_3), is not fluxional and has the shortest Si-N distance of this series, apparently nitrogen coordination when sufficiently strong acts to inhibit the exchange process.[2]

SUMMARY AND CONCLUSION

It is clear that silatranes constructed with six-membered rings impart structural flexibility that allows substituent effects to be studied with far greater ease than that with previously studied silatranes which contained five-membered rings. This is borne out by both the wide range in Si-N distances that are observed (from X-ray structural studies) and ^{29}Si chemical shifts that readily correlate with electronic effects of attached axial substituents for the silatranes with six-membered rings.

Acknowledgment

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