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# Synthesis and characterization of (4*S*)-silatrane-4-carboxylic acids; molecular structure of (3*R*,4*S*)-1-vinyl-3-methylsilatrane-4-carboxylic acid *

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## Abstract

A new class of silatrane compounds, (4*S*)-(–)-silatrane-4-carboxylic acids **I–IV**, was synthesized by the transesterification of organyltriethoxysilanes with L-*N*,*N*-bis(2-hydroxyethyl)serine or L-*N*,*N*-bis(2-hydroxyethyl)threonine in the presence of a catalytic amount of pyridine. The compounds were characterized by IR spectra, $^{1}H$, $^{13}C$ and $^{29}Si$ NMR spectra and mass spectra as well as by elemental analyses. The results indicate that the transannular Si ← N dative bond is present. The IR spectra indicated that there are two tautomers, acid form and salt form, in these compounds, with the acid form predominant. The crystal structure of (3*R*,4*S*)-(–)-1-vinyl-3-methylsilatrane-4-carboxylic acid was determined by X-ray diffraction. The Si ← N bond distance is 2.169(3) Å.

## 1. Introduction

The five-coordinated silicon compounds, silatranes (2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecanes) have attracted much attention because of their peculiar structures and wide variety of biological activities [1]. A great number of silatrane compounds has been synthesized and studied since the early 1960s [2]. In the present paper, we report a new class of silatrane compounds, (4*S*)-(–)-1-substituted silatrane-4-carboxylic acids and (3*R*,4*S*)-(–)-1-substituted-3-methylsilatrane-4-carboxylic acids. These were synthesized by the transesterification of organyltriethoxysilanes with L-*N*,*N*-bis(2-hydroxyethyl)serine or L-*N*,*N*-bis(2-hydroxyethyl) threonine. The structure of these 4-carboxyl substituted silatranes and the influence of the carboxyl group on the transannular Si ← N dative bond were also studied. The Si ← N dative bond has been found to be stronger than the interaction of carboxylic acid with tertiary amine.

## 2. Results and discussion

### 2.1. *Synthesis of 1-substituted silatrane-4-carboxylic acids*

(4*S*)-(–)-1-methylsilatrane-4-carboxylic acid (**I**) and (4*S*)-(–)-1-vinylsilatrane-4-carboxylic acid (**III**) were synthesized by the transesterification of methyltriethoxysilane or vinyltriethoxysilane with L-*N*,*N*-bis(2-hydroxyethyl)serine in the presence of pyridine. (3*R*,4*S*)-(–)-1,3-Dimethylsilatrane-4-carboxylic acid (**II**) and (3*R*,4*S*)-(–)-1-vinyl-3-methylsilatrane-4-carboxylic acid (**IV**) were similarly prepared by reacting with L-*N*,*N*-bis(2-hydroxyethyl)threonine.

| Compound | R | R′ |
|---|---|---|
| **I** | Me | H |
| **II** | Me | Me |
| **III** | vinyl | H |
| **IV** | vinyl | Me |

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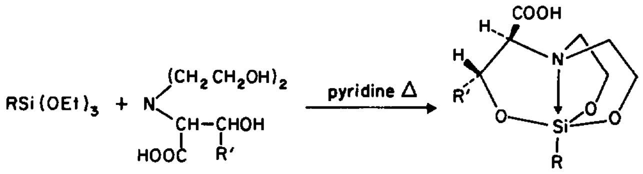
TABLE 1. Yields, melting points, specific rotations and analytical data for 1-substituted silatrane-4-carboxylic acids

| Compound | Yield (%) | M.p. (°C) | Specific rotation [a] | Anal. (found (calc.) (%)) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| I | 82 | 162 | − 55.5 | 40.87 | 6.54 | 5.81 |
| | | (dec) | (25, 3.47) | (41.20) | (6.44) | (6.01) |
| II | 35.7 | 178–180 | − 97.9 | 43.15 | 7.24 | 5.34 |
| | | | (25, 5.62) | (43.72) | (6.88) | (5.76) |
| III | 72 | 260 | − 116 | 44.36 | 6.50 | 5.39 |
| | | (dec) | (23, 4.02) | (44.08) | (6.12) | (5.71) |
| IV | 67.5 | 202–204 | − 118.5 | 46.44 | 5.36 | 6.81 |
| | | | (22, 6.66) | (46.31) | (5.40) | (6.61) |

[a] Specific rotation $[\alpha]_D^t$ with temperature (°C) and concentration in DMSO ($\times 10^{-3}$ g ml$^{-1}$).



In the absence of pyridine, the transesterification can barely proceed under the usual reaction conditions. This is probably due to the existence of the zwitterionic form of the dihydroxyethylated amino acid, and the protonated amine being unable to form the Si ← N dative bond. It seems most likely that the catalytic mechanism of pyridine in this reaction is to restore the lone-pair electrons of the nitrogen and thus facilitate the formation of the transannular Si ← N dative bond and the consequent silatrane ring. On the other hand, pyridine can also increase the miscibility of the reactants in the reaction.

There are three hydroxyalkyl groups and a carboxyl group in L-*N*,*N*-bis(2-hydroxyethyl)serine or threonine. Both the hydroxyalkyl group and the carboxy group are able to form the Si–O bond by replacement of the ethoxy group in triethoxysilanes. The reaction of organyltriethoxysilanes with the ligands produces 1-organylsilatrane-4-carboxylic acids because the Si–O bond with the alkoxy oxygen is more readily formed than that with the carboxyl oxygen [3].

All (4*S*)-silatrane-4-carboxylic acids are white crystalline substances. Their melting points, specific rotations, yields and elemental analyses are listed in Table 1.

### 2.2. *Infrared spectroscopy*

The characteristic absorptions of silatrane-4-carboxylic acids I–IV are listed in Table 2. The absorption bands in the region of 1738–1728 cm$^{-1}$ are attributed to the carboxyl C=O groups. These absorption frequencies are lower than that of the C=O (*Ca.* 1750 cm$^{-1}$) in silatrane-3-ones [4]. It is interesting to point out that a weak absorption band in the range of 1645–1635 cm$^{-1}$ is also observed co-existent with the strong carboxylic acid C=O group absorption band in all cases, as shown in Fig. 1. On the other hand, the values of these

TABLE 2. Characteristic absorptions of compounds I–IV (cm$^{-1}$, KBr)

| Compound | ν(O–H) | ν(C=O) | ν(C=C) | ν(C–O) | ν(Si–O) | ν(Si–C) | ν(C–N) |
|---|---|---|---|---|---|---|---|
| I | 3492m | 1728vs | – | 1088s | 688s | 639s | 905s |
| | 940s | 1637w | | 1116s | 831vs | | 940s |
| | | | | 1218s | 1032s | | |
| II | 3480m | 1738vs | – | 1098s | 678s | 646s | 912s |
| | 962s | 1645w | | 1132s | 825vs | | 928s |
| | | | | 1219vs | 1028s | | |
| III | 3452m | 1733s | 1607w | 1085vs | 688s | 630s | 902s |
| | 954s | 1642w | | 1132s | 746vs | | 937s |
| | | | | 1215vs | 1031s | | |
| IV | 3415m | 1733vs | 1598w | 1080s | 680s | 635m | 900m |
| | 954s | 1630w | | 1122vs | 762vs | | 918m |
| | | | | 1208vs | 1013s | | |

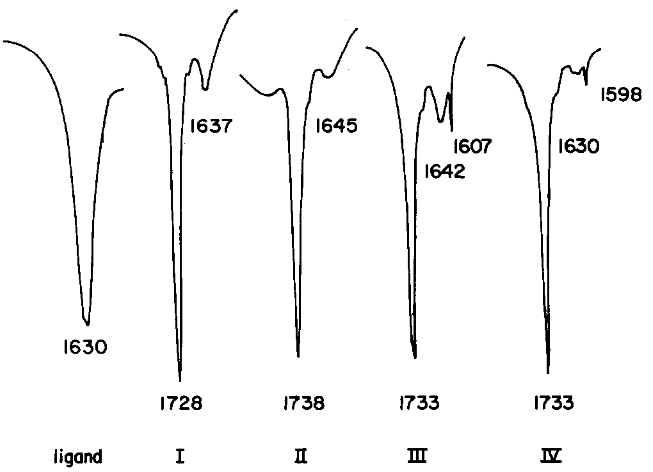
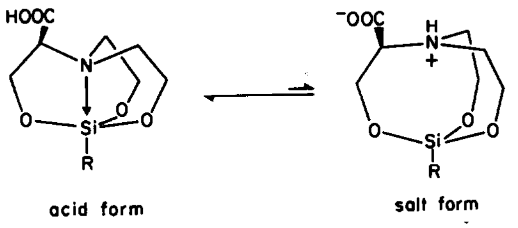


Fig. 1. The IR spectra of L-$N,N$-bis(2-hydroxyethyl)serine and compounds I–IV in the region of 1550–1800 $cm^{-1}$.

absorption frequencies are almost identical with that of the dipolar or zwitterion form of L-$N,N$-bis(2-hydroxyethyl)serine (1630 $cm^{-1}$). Therefore, we suggest that the silatrane-4-carboxylic acid offers the possibility of tautomerism to a salt form. One tautomer has a free carboxyl group (acid form), the other a zwitterion (salt form), and they are in equilibrium. The relative abundance of the tautomers can be roughly estimated from the intensities of the two absorption bands, and hence the acid form tautomer is predominant. Furthermore, it is to be expected that the salt form tautomer results in the weakening of the Si ← N dative bond in silatrane framework.



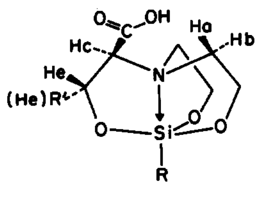
### 2.3. NMR spectroscopy

The $^1H$, $^{13}C$ and $^{29}Si$ NMR chemical shifts of the four compounds are given in Table 3. The introduction of a carboxyl group in the 4$S$ position (I and III) or of both a methyl group in the 3$R$ and a carboxyl group in the 4$S$ position of silatrane (II and IV) distorts the $C_3$ symmetry of the silatrane framework, and makes the proton NMR spectra of the atrane species much more complicated. The proton signals of the substituted chain shift to a lower field than that of the two unsubstituted chains. The protons on the two unsubstituted chains are not equivalent. The chemical shift of the $NCH_2$ protons is close to that of the simple silatrane and implies the presence of a transannular Si ← N bond in these silatrane-4-carboxylic acids [5].

The signals of NC and CO carbons in the substituted chain also shift to a lower field than of those in unsubstituted chains. It seems that the NC and CO carbons in the unsubstituted chains are not influenced by the presence of the carboxyl group in compounds I and III. However the carbons in the unsubstituted chains are affected by the steric hindrance caused by

TABLE 3. $^1H$, $^{13}C$ and $^{29}Si$ chemical shifts in the NMR spectra of 1-substituted silatrane-4-carboxylic acids

| Compound | $^1H$, $^{13}C$ chemical shifts, $\delta$, ppm, in DMSO-$d_6$ | | | | | | | | $^{29}Si$ |
|---|---|---|---|---|---|---|---|---|---|
| | Si–R | $NCH_2$ + $NCH_b$ | $NCH_a$ | $NCH_c$ | $OCH_2$ | $OCH_{2e}$ or $OCH_e$ | $CH_3$ | COOH | |
| I | −0.35s<br>−2.38 | 2.76m<br>54.1 | 3.07m | 3.75m<br>58.7 | 3.59m<br>57.2 | 3.78m<br>67.2 | | <br>169.6 | −55.8 |
| II | −0.36s<br>0.10 | 2.73m<br>48.3, 49.4 | 3.09m | 3.15d<br>64.7 | 3.60m<br>57.2 | 3.81m<br>65.8 | 1.20d<br>21.0 | <br>171.0 | −74.2 |
| III | 5.57m<br>135.0<br>133.9 | 2.81m<br>54.1 | 3.14m | 3.80m<br>58.7 | 3.60m<br>57.2 | 3.85m<br>67.2 | | <br>169.6 | −70.6 |
| IV | 5.57m<br>141.9<br>128.3 | 2.80m<br>48.5, 49.5 | 3.15m | 3.22d<br>64.7 | 3.65m<br>57.1<br>57.2 | 3.89m<br>65.7 | 1.23d<br>21.1 | <br>170.7 | −89.5 |



the methyl and carboxyl groups in compounds **II** and **IV**. The two $NCH_2$ carbons are not equivalent and shift upfield compared with the former two compounds. In the $^{13}C$ NMR spectrum of **IV**, we have found that the two $OCH_2$ carbons are slightly different too.

The substituents on the framework also have a significant influence on the chemical shift of the silicon. The resonances of $^{29}Si$ of compounds I and III shift to a higher field than those of the corresponding organyltriethoxysilanes [6], but to a lower field than those of methyl and vinyl silatranes [7]. Many studies on $^{29}Si$ NMR spectra of silatranes have indicated that the increase of the absolute value of chemical shift of silicon in silatranes (as compared with organyltriethoxysilanes) correlates with the degree of transannular Si ← N interaction [6–8]. Thus, the above comparison suggests that the molecules of **I** and **III** have the dative Si ← N bond in solution, but it is weaker than that of the corresponding silatrane. This may be due to the weakening of Si ← N bond in solution. However, in the case of compounds **II** and **IV**, the situation is very different. The absolute values of $^{29}Si$ are higher than those of organyltriethoxysilanes and organylsilatranes as well. It seems that these molecules have a stronger Si ← N dative bond, opposite to the result obtained from $^{29}Si$ NMR spectra of **I** and **III**. The high field shift of $^{29}Si$ in compounds **II** and **IV** may be regarded not only as dependent on the degree of Si ← N interaction but also on the steric effect of the two substituents.

TABLE 4. The characteristic peaks ($m/e$, %) in the EI mass spectra of compounds **I–IV**

| Ion | $m/e$ (abundance relative to the base ion peak (%)) | | | |
|---|---|---|---|---|
| | **I** | **II** | **III** | **IV** |
| $M^{+\cdot}$ | 233(17.5) | 247(5.3) | 245(9.6) | 259(4.1) |
| [M–R]+ | 218(36.0) | 232(31.6) | 218(100) | 232(100) |
| $[M-CO_2H]+$ | 188(100) | | 200(21.1) | |
| $[M-CO_2]+$ | | 203(50) | | 215(27.6) |
| $[M-R-CO_2]+$ | 174(5.3) | 188(3.5) | 174(5.3) | 188(10.6) |
| $[M-CO_2H-RH]+$ | 172(14) | 186(2.6) | 172(9.6) | 186(10.6) |
| $[M-CO_2H-OCH_2]+$ | 158(19.3) | | 170(5.3) | |
| $[M-CO_2-R-OCH_2]+$ | 144(19.3) | 158(32.5) | 144(7.0) | 158(6.1) |
| $[N(CH_2CH_2OH)_3]+$ | 149(46.5) | 149(6.1) | 149(52) | 149(18.6) |
| $[SiC_4H_{10}O_2N]+$ | 132(38.6) | 132(100) | 132(8.8) | 132(4.1) |

### *2.4. Mass spectroscopy*

The characteristic ions in the electron-impact mass spectra of 1-substituted silatrane-4-carboxylic acids are summarized in Table 4. The molecular ion peaks are found in the spectra of all compounds, in which their relative abundances vary from 3.3 to 17.5%. The most abundant peak, corresponding to the silatrane framework, arises from either the loss of a carboxyl group ($[M-COOH]^+$ or $[M-CO_2]^+$) or the cleavage of the Si–R bond ($[M-R]^+$) depending on the substituents on silicon and on the ring except for compound **II**. The most abundant peak in the spectrum of **II** is $[SiC_4H_{10}O_2N]^+$ which may be produced by a ring rupture process. The ions produced by the ring rupture are also present in the spectra of other compounds in different abundances. The presence of the carboxyl group on the ring may affect the stability of the silatrane framework towards electron impact. The presence of a methyl group in the $\beta$ position of carboxyl group in **II** and **IV** leads to a unique loss of $CO_2$ which is different from the loss of carboxyl group in **I** and **III**.

### *2.5. Molecular and crystal structure*

The perspective view and the framework viewed down the N → Si bond of (3*R*,4*S*)-(–)-vinyl-3-methylsilatrane-4-carboxylic acid is shown in Fig. 2 with numbering of atoms. Atomic positions and estimated deviations are listed in Table 5. Bond distances and bond

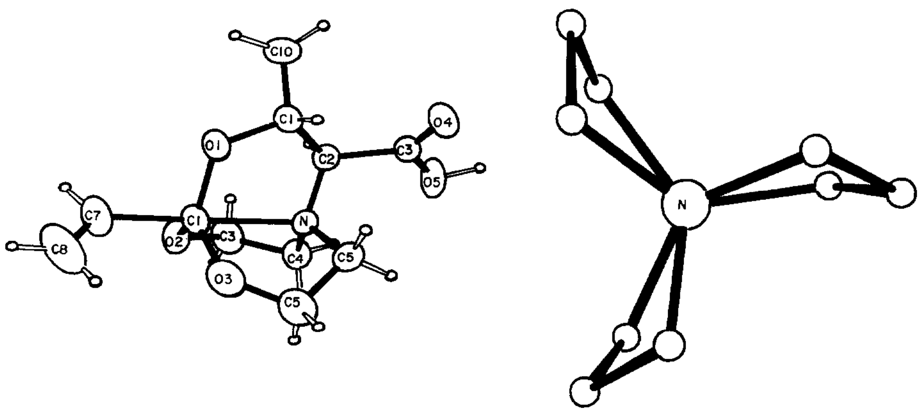


Fig. 2. The perspective view and the framework viewed down N–Si axis.

TABLE 5. The atomic positions and estimated deviations of IV

| Atom | *x* | *y* | *z* | *B* (Å$^2$) |
|---|---|---|---|---|
| Si | 0.4668(2) | 0.8996(1) | 0.2723(8) | 2.56(2) |
| O1 | 0.5859(5) | 0.7882(2) | 0.2474(7) | 3.14(7) |
| O2 | 0.5880(5) | 1.0033(3) | 0.3186(2) | 3.07(7) |
| O3 | 0.2696(5) | 0.9290(3) | 0.2177(2) | 3.85(7) |
| O4 | 0.7699(6) | 0.8011(3) | −0.0265(2) | 3.95(8) |
| O5 | 0.8601(5) | 0.9720(3) | −0.0035(2) | 3.88(7) |
| N | 0.5933(5) | 0.9577(3) | 0.1456(2) | 2.14(7) |
| C1 | 0.6796(7) | 0.7693(4) | 0.1621(3) | 2.71(9) |
| C2 | 0.7422(6) | 0.8795(3) | 0.1255(3) | 2.23(8) |
| C3 | 0.7205(7) | 1.0649(4) | 0.2673(3) | 3.4(1) |
| C4 | 0.6593(7) | 1.0684(4) | 0.1683(3) | 3.1(1) |
| C5 | 0.2649(8) | 0.9839(6) | 0.1315(4) | 5.0(1) |
| C6 | 0.4377(7) | 0.9541(4) | 0.0787(3) | 3.5(1) |
| C7 | 0.3639(7) | 0.8494(4) | 0.3836(4) | 4.2(1) |
| C8 | 0.1906(1) | 0.8386(5) | 0.4051(5) | 7.1(2) |
| C9 | 0.7921(6) | 0.8770(4) | 0.0231(3) | 2.46(9) |
| C10 | 0.8419(8) | 0.6948(4) | 0.1778(4) | 4.2(1) |
| H1 | 0.598 | 0.732 | 0.117 | 5 |
| H2 | 0.855 | 0.902 | 0.157 | 5 |
| H3a | 0.841 | 1.032 | 0.271 | 5 |
| H3b | 0.728 | 1.137 | 0.292 | 5 |
| H4a | 0.560 | 1.121 | 0.159 | 5 |
| H4b | 0.761 | 1.090 | 0.128 | 5 |
| H5a | 0.264 | 1.062 | 0.141 | 5 |
| H5b | 0.156 | 0.966 | 0.097 | 5 |
| H6a | 0.424 | 0.884 | 0.053 | 5 |
| H6b | 0.459 | 1.004 | 0.029 | 5 |
| H7 | 0.451 | 0.830 | 0.432 | 5 |
| H8a | 0.144 | 0.813 | 0.461 | 5 |
| H8b | 0.095 | 0.857 | 0.356 | 5 |
| H9 | 0.918 | 0.971 | −0.063 | 5 |
| H10a | 0.868 | 0.649 | 0.125 | 5 |
| H10b | 0.953 | 0.735 | 0.191 | 5 |
| H10c | 0.804 | 0.650 | 0.232 | 5 |

angles are listed in Tables 6 and 7 respectively. The silicon atom in the crystal has a distorted trigonal bipyramidal coordination with three alkoxy oxygen atoms in the equatorial positions and a nitrogen atom and a carbon atom in the axial positions, and the carboxyl oxygen free from coordination to the central atom. The molecule shows a typical atrane feature and the carboxyl group on the ring causes no significant changes in the structure of the atrane framework, and in particular, in the transannular coordination of nitrogen to silicon. The transannular Si ← N bond length is 2.169(3) Å, longer than that in 1-vinylsilatrane (2.150 Å) [9], much shorter than that of PtCl-$[Si(OCH_2CH_2)_3N][PMe_2Ph]_2$ (2.89(1) Å) [10]. The N–Si–C bond angle is 178.4(2)°, very close to the value in 1-vinylsilatrane (178.7(2)°). The C=C bond distance is 1.284 Å, shorter than that of ethylene (1.34 Å) due to the dative Si ← N interaction. The torsional angle N–Si–C7–C8 of −169.7° indicates that the vinyl group and Si, N atoms deviate slightly from planar and an influence of the Si ← N dative interaction on the vinyl group is possible, causing the C=C bond to be shorter than normal [11].

## 3. Experimental details

Solvents were purified by standard methods. IR spectra were recorded with a Shimadzu IR-440 spectrometer, $^1H$, $^{13}C$ and $^{29}Si$ NMR spectra with a Varian XL-200 NMR spectrometer, EI mass spectra with a VG ZAB-HF-3F spectrometer and elemental analyses

TABLE 6. Bond distances (Å)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Si–O1 | 1.656(3) | N–C4 | 1.482(5) | Si–O2 | 1.685(3) | N–C6 | 1.476(7) |
| Si–O3 | 1.656(3) | C1–C2 | 1.526(6) | Si–N | 2.169(3) | C1–C10 | 1.496(7) |
| Si–C7 | 1.878(5) | C2–C9 | 1.526(6) | O1–C1 | 1.426(5) | C3–C4 | 1.502(7) |
| O2–C3 | 1.424(6) | C5–C6 | 1.498(8) | O3–C5 | 1.421(7) | C7–C8 | 1.284(10) |
| O5–C9 | 1.327(5) | O4–C9 | 1.192(5) | N–C2 | 1.465(6) | | |

TABLE 7. Bond angles (°)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1–Si–O2 | 116.9(2) | C4–N–C6 | 114.4(3) | O1–Si–O3 | 121.0(2) | C2–N–C6 | 113.3(3) |
| O1–Si–N | 82.9(1) | O1–C1–C10 | 109.4(4) | O1–Si–C7 | 96.9(2) | O1–C1–C2 | 107.0(3) |
| O2–Si–O3 | 117.5(2) | N–C2–C1 | 107.8(4) | O2–Si–N | 82.7(1) | C2–C1–C10 | 111.9(4) |
| O2–Si–C7 | 96.2(2) | C1–C2–C9 | 112.8(3) | O3–Si–N | 83.0(2) | N–C2–C9 | 112.1(3) |
| O3–Si–C7 | 98.6(2) | N–C4–C3 | 106.1(3) | N–Si–C7 | 178.4(2) | O2–C3–C4 | 108.7(4) |
| Si–O1–C1 | 124.5(3) | N–C6–C5 | 106.1(4) | Si–O2–C3 | 122.6(3) | O3–C5–C6 | 108.3(5) |
| Si–O3–C5 | 123.0(3) | O4–C9–O5 | 124.5(4) | Si–N–C2 | 104.7(2) | Si–C7–C8 | 128.3(5) |
| Si–N–C4 | 104.5(2) | O5–C9–C2 | 110.9(4) | Si–N–C6 | 103.5(3) | O4–C9–C2 | 124.9(4) |
| C2–N–C4 | 114.9(4) | | | | | | |

with a Carlo-Erba 1106 elemental analyzer. The specific rotations were measured on a Spoif WZZ-2 automatic polarimeter with a 2 dm tube using DMSO as solvent. L-*N*,*N*-Bis(2-hydroxyethyl)serine and L-*N*,*N*-bis(2-hydroxyethyl)threonine were synthesized from the reaction of 2-chloroethanol with L-serine and L-threonine respectively [12].

Preparation of **I**. A mixture of methyltriethoxysilane (1.0 g, 5.6 mmol), L-*N*,*N*-bis(2-hydroxyethyl)serine (1.0 g, 5.3 mmol) and a catalytic amount of pyridine was stirred at 70–80°C for *ca.* 8 h. After the solid was completely dissolved, the ethanol formed was distilled off under vacuum. The residue was dissolved in tetrahydrofuran (THF) and precipitated by petroleum ether (30–60°C). The product was recrystallized from THF and petroleum ether to give white crystals 1.0 g.

**II–IV** were prepared according to the same procedure.

### *3.1. X-ray structure determination*

The X-ray diffraction data were measured on a computer controlled CAD4 (Enraf-Nonius) diffractometer at room temperature. Crystal data, data collection and least-squares parameters are listed in Table 8.

TABLE 8. The crystal data, data collection and least-squares parameters of **IV**

| | |
|---|---|
| Empirical formula | $SiO_5C_{10}H_{17}N$ |
| M | 259.34 |
| Crystal system | orthorhombic |
| $F(000)$ | 552 |
| $a$ (Å) | 7.142(6) |
| $b$ (Å) | 12.336(8) |
| $c$ (Å) | 14.497(3) |
| $V$ (Å$^3$) | 1277.3 |
| Space group | $P2_12_12_1$ |
| $Z$ | 4 |
| $D_x$ (g cm$^{-3}$) | 1.349 |
| $\lambda$(Mo K$\alpha$) (Å) | 0.71073 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 1.856 |
| $\theta_{max}$(°) | 25 |
| Scan technique | $\theta/2\theta$ |
| No. of unique data | 1315 |
| Reflections used in least squares (NO) | 1013 ($I > 3\sigma(I)$) |
| Number of variables | 154 |
| $R_1$ | 0.036 |
| $R_2$ | 0.039 |

The structure of (3*R*,4*S*)-(−)-1-vinyl-3-methylsilatrane-4-carboxylic acid was solved by direct methods by using the MULTAN program and refined anisotropically by full-matrix least-squares for non-hydrogen atoms. Positional parameters of the hydrogen atoms were located from difference Fourier syntheses and refined isotropically. All calculations were performed by PDP11/44 computer using the SDP program.

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