1 Introduction

The search for organic materials for non-linear optics (NLO) has revealed quite many compounds with high efficiency for frequency doubling of laser light, but they suffer from a lack of transparency. This is due to the generally accepted design of a NLO material which consists in connecting a donor and an acceptor group by a conjugated bridge which leads to highly coloured materials. To avoid the problems with this approach, we started to develop compounds whose hyperpolarizability relies on the existence of weak bonds. Here, the *silatranes* represent a well-studied class of stable molecules with a weak Si-N bond. Silatranes (2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecanes) are a special case of pentacoordinate silicon with unusal properties which have gained considerable interest over the last decades [1, 2, 3, 4]. Interestingly, the silicon-nitrogen bond is ignored in the name used by Chemical Abstracts (it should rather be a tricyclic system).

We introduced *chirality* as only compounds which crystallize in non-centrosymmetric space groups give non-vanishing hyperpolarizabilities as bulk materials, e.g. in crystalline form, which is important for applications in devices. Only very few silatranes with a chiral backbone are known up to now [5, 6]. Starting with (1S)-β-pinene as the source of chirality, we have prepared such a chiral silatrane and characterized it by X-ray structure analysis [7].

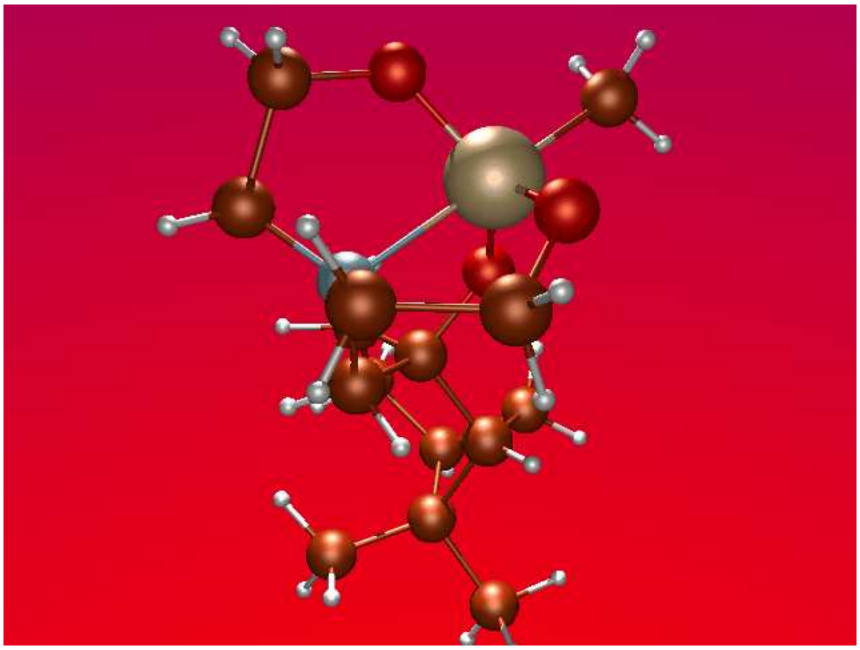


Figure 1: X-Ray structure of our chiral silatrane

2 Experimental

2.1 Synthesis of the chiral triethanolamine: (1R,2S)-2-[N,N-bis(2-hydroxyethyl)-aminomethyl]-6,6-dimethyl-2-hydroxybicyclo[3.1.1]heptane

A mixture of diethanolamine (1.05 g, 10 mmol) and (1R,2S)-β-pinene epoxid [8] (1.52 g, 10 mmol) was stirred at 120°C for 2 days. Volatile impurities were distilled off at 120°C (6mm). The residual yellow oil was used without further purification.

Yield 95 %; HPLC-ESI: m/e 257 (M^+); calculated for $C_{14}H_{27}NO_3$: 257.37.

Figure 2: Synthesis of the chiral silatrane

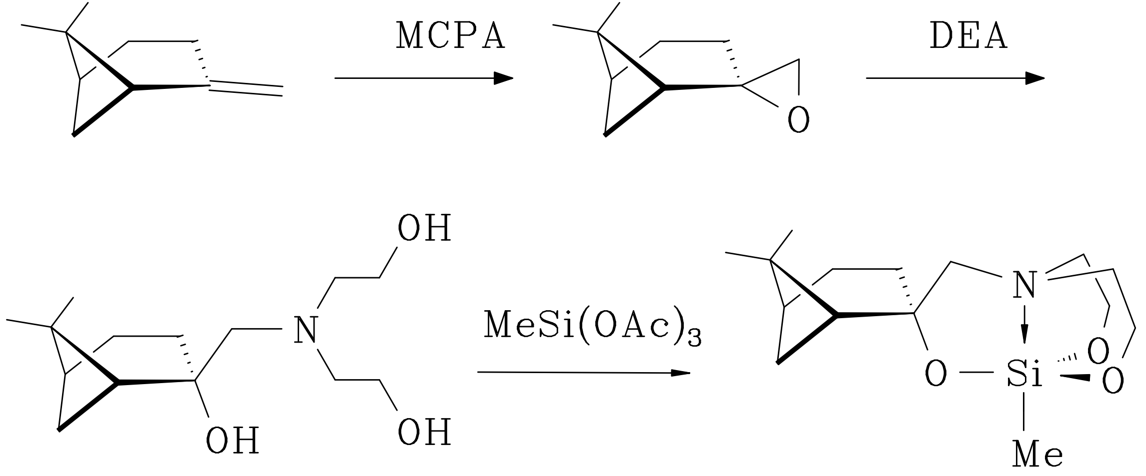


Table 1: ^{1}H NMR ($CDCl_3$) for **2**(for numbering see figure 3)

δ (ppm)	mult.	J (Hz)	Int.	assignment
0.95	s		3H	9 (anti to C-7)
1.25	s		3H	8 (syn to C-7)
1.51	d	9.15	1H	7 (anti to CMe_2)
1.66	m		1H	6
1.78	m		1H	5
1.80	m		1H	6
1.89	m		1H	4
1.93	m		1H	5
2.16	m		1H	2
2.17	m		1H	7 (syn to CMe_2)
2.54	d	14.0	1H	10
2.70	d	14.0	1H	10
2.64, 2.76	m, m		4H	12 and 14
3.58, 3.68	m, m		4H	11 and 13
3.60	s (br)		3H	OH

Table 2: ^{13}C NMR ($CDCl_3$) for**2**(for numbering see figure 3)

δ (ppm)	mult.	assignment
23.83	CH_3	9
25.06	CH_2	5
27.25	CH_2	7
27.46	CH_3	8
29.48	CH_2	6
38.06	C_q	3
40.96	CH	4
50.30	CH	2
59.01	$2 \times CH_2$	12 and 14
60.05	$2 \times CH_2$	11 and 13
66.78	CH_2	10
76.21	C_q	1

2.2 Synthesis of the methylsilatrane: (1*R*,2*S*)-1',6,6-trimethyl-spiro[bicyclo[3.1.1]heptane-2,3'-5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3]undecane]

A mixture of trichloro-methylsilane (374 mg, 2.5 mmol), acetic anhydride (776 mg, 7.8 mmol) and NaOAc (50 mg, 0.6 mmol) was kept at 60°C for 4 h. Acetyl chloride and excess of acetic anhydride was distilled off at 6 mm. The residue was dissolved in $CHCl_3$ (10 ml), cooled to 0°C, and then a solution of the chiral triethanolamine (643 mg, 2.5 mmol) in $CHCl_3$ (20 ml) was added dropwise within 30 min. The reaction mixture was stirred at room temperature for 12 h, the solvent evaporated, and the residue chromatographed on silica gel/CH_2Cl_2:ethylacetate=10:1. The corresponding product was obtained as a white solid. X-ray quality crystals were grown by slow evaporation of a solution in CH_2Cl_2/Et_2O at room temperature.

Yield 270 mg (36 %); HPLC-ESI *m/e* 297 (M^+); calculated for $C_{15}H_{27}NO_3Si$: 297.47.

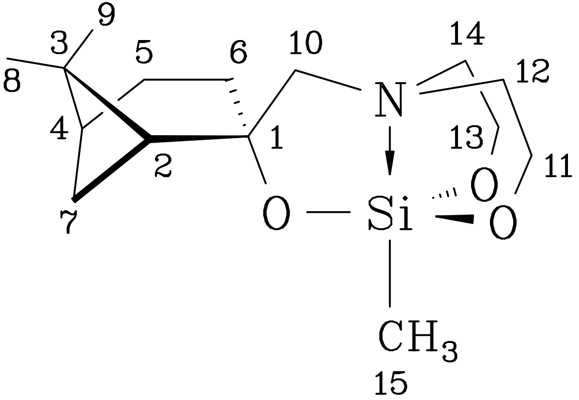
Table 3: ^{1}H NMR ($CDCl_3$) for**1**(for numbering see figure 3)

δ (ppm)	mult.	J (Hz)	Int.	assignment
-0.14	s		3H	15
0.90	s		3H	9 (anti to C-7)
1.22	s		3H	8 (syn to C-7)
1.62	d	10.4	1H	7 (anti to CMe_2)
1.76	m		1H	5
1.87	m		1H	6
1.88	m		1H	4
1.93	m		1H	2
1.95	m		1H	5
2.07	m		1H	6
2.15	m		1H	7 (syn to CMe_2)
2.75	d	13.5	1H	10
2.78	m		3H	12 or 14
2.85	d	13.5	1H	10
2.91	m		1H	12 or 14
3.73	m		2H	11 or 13
3.74	m		2H	11 or 13

Table 4: ^{13}C NMR ($CDCl_3$) for **1**(for numbering see figure 3)

δ (ppm)	mult.	assignment
-0.85	CH_3	15
23.64	CH_3	9
25.09	CH_2	5
27.30	CH_2	7
27.40	CH_3	8
34.30	CH_2	6
37.54	C_q	3
40.29	CH	4
54.11	CH_2	12 or 14
54.72	CH	2
54.72	CH_2	12 or 14
57.70	CH_2	11 or 13
57.90	CH_2	11 or 13
64.55	CH_2	10
76.58	C_q	1

Figure 3: Structure and numbering scheme for **1**.



3 Topological analysis of the electron density

3.1 Introduction

In contrast to almost all other derivatives of silicic acid, silatranes are remarkably stable towards hydrolysis. This feature was traced back to the *hypervalency* of the silicon which has not only three bonds to oxygen and one to carbon, but shows, according to crystal structures, a quite low distance to nitrogen which might be interpreted as a fifth bond. The structure with a low Si-N distance (*endo*-structure, around 2.2Å) is expected to be more stable than the corresponding *exo*-species (Si-N distance around 2.6Å), where a direct interaction between nitrogen and silicon should be much weaker. The nature of this weak Si-N bond was the target of a great number of calculations [9]. *Csonka* and *Hencsei* have shown that at sufficient level of theory the pentacoordinate *endo*-species is the only energetic minimum on the potential surface, [10, 11], although the surface seems to be very flat in the direction of the Si-N vector. *Gordon* performed a Bader analysis for several silatranoles [12] finding an ionic interaction between silicon and nitrogen, as well as between silicon and oxygen. These calculations were performed on AM1-optimised structures, which give only a rough approximation of solid state properties. In particular, they give considerably longer Si-N distances than observed in crystal structures (but more close to the experimental gas phase values).

We performed a number of calculations on the X-ray geometry of our chiral silatrane derived from (S)-β-pinene using the AIMPAC[1] package [13, 14] for topological analysis. To our knowledge, it is the first topological analysis of a chiral silatrane.

For a detailed explanation of the theory of topological analysis and the terminology used, see Bader's website[2].

3.2 Gradient field analysis

The analysis of the electron density as introduced by Bader gives a mathematically stringent definition of a chemical bond. The existence of a bond is indicated by the presence of a so-called **bond critical point** (bcp). This is a saddle point ($\nabla\rho(r) = 0$) in the electron density between two nuclei, where the Hessian (the second derivative matrix) of the electron density has one positive eigenvalue in the bond axis and two negative eigenvalues perpendicular to the bond axis. From this follows that there exists a path of maximum electron density from one nucleus to another passing through the bond critical point [15]. This path is called "the bond".

We determined some bond critical points and bond paths for our chiral silatrane. The bond paths are visualised in figure 4 and the properties of the critical points are summarised in table 5. Figure 4 shows clearly the bond path between silicon and nitrogen, as well as the path between silicon and oxygen. The bond critical

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[1] http://www.chemistry.mcmaster.ca/faculty/bader.html

[2] http://www.chemistry.mcmaster.ca/faculty/bader.html

points are the crossing points of the bond path (blue) and the interatomic surface (zero-flux surface, green) (for a definition, see below).

Figure 4: Gradient field of the core of our chiral silatrane in a plane defined by Si(1), O(2) and N(5) (red: gradient paths, blue: bond path, green: zero-flux path)