Journal of Organometallic Chemistry, 418 (1991) 173–182
Elsevier Sequoia S.A., Lausanne

JOM 21990

The effect of ring substitution on the geometry of the silatrane skeleton: the crystal structures of 1-phenyl-3,7,10-trimethylsilatrane and 1-*p*-tolyl-carbasilatrane

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(Received April 23rd, 1991)

Abstract

The crystal structures of 1-phenyl-3,7,10-trimethylsilatrane (I) and 1-*p*-tolyl-carbasilatrane (II) were determined by X-ray diffraction. Both compounds crystallize with two independent molecules in the asymmetric unit. I ($\bar{d}$(Si ← N) = 2.175(6) Å) is the minor stereoisomer fraction of the diastereomer mixture possessing approximate C_3 symmetry. The conformation of the silatrane moiety is different from that observed in the major (asymmetric) structure of *p*-tolyl-trimethylsilatrane. The mean Si ← N distance in II (2.290(2) Å) is identical with the bond length observed for the phenyl derivative. The dative bond lengths in various silatranes and silatrane analogs are compared.

Introduction

Extensive structural studies on silatranes [$RSi(OCH_2CH_2)_3N$] and their derivatives established that the length of the dative Si ← N bond primarily depends on the electron withdrawing nature of the apical substituent R [1]. Changing the structure of the silatrane skeleton, normally possessing approximate three-fold (C_3) symmetry, may also affect the dative bond between the five-coordinated silicon and the nitrogen atom. The substitutions on the silatrane skeleton, on the one hand, change the electron density on the silicon atom, and on the other hand, they distort this moiety and introduce steric interactions. Significant shortening of the dative bond was observed for silatranones [2,3] and silatrane-diones [4] caused by the carbonyl groups at 3 and 3,7 positions. 3,7,10-Alkyl substitution, which leads to mixtures of stereoisomers, causes dramatic changes in the conformation of the silatrane skeleton. The three-fold symmetry is distorted in the major fraction of the *p*-tolyl-trimethyl derivatives [5]. The presence of both electron and steric factors is detected

0022-328X/91/$03.50

for molecules in which one of the ethoxy bridges is substituted by a propyl bridge (carbasilatranes) [6].

Numerous crystal structures available for silatranes involve aryl substituents in 1-positions. The electronic effects of these substituents are fairly similar, facilitating the comparison of the molecular geometries. In the present study we synthesized and separated the minor fraction of an aryl-3,7,10-trimethyl silatrane I [$C_6H_5Si(OCH(CH_3)CH_2)_3N$], and synthesized an aryl-carbasilatrane II [*p*-$CH_3C_6H_4Si(CH_2CH_2CH_2)(OCH_2CH_2)_2N$]. The crystal structures of these derivatives were compared to those available in the literature. An attempt was made to clarify the effects of these substitutions on the molecular geometries.

Experimental

Synthesis

I was synthesized by *trans*-esterification of phenyl-trimethoxysilane and tri-isopropanolamine in xylene [7]. The compound was purified by recrystallization from benzene, m.p. 131–133 °C (133–134 °C [7]). The stereoisomers were separated by HPLC (Chromsil C 18 normal phase column, CH_2Cl_2 eluent, UV detector, 254 nm). The new compound II was synthesized according to Lukevics et al. [8] from dimethoxysilane and diethanolamine (xylene solution, triethylamine as HCl acceptor). The compound was recrystallized from n-heptane, m.p. 84–85 °C, yield 38%. Anal. Found: C, 63.48; H, 8.10; N, 4.75; Si, 10.42. $C_{14}H_{21}NO_2Si$ calc.: C, 63.84; H, 8.04; N, 5.32; Si, 10.66%. ^1H NMR data (ppm/TMS): 3.81 (m, OCH_2); 2.79 (t, NCH_2); 2.72 (t, NCH_2); 1.71 (qui, C–CH_2C); 0.80 (t, $SiCH_2$).

Crystal structure determinations

Crystals of I and II were mounted on an Enraf–Nonius CAD4 four-circle computer controlled single crystal diffractometer equipped with an incident beam graphite monochromator and Ni-foil attenuator. Unit cell parameters were determined from the setting angles of 25 carefully centered reflections (range: I, $22 < \theta < 25°$; II, $38 < \theta < 39°$). Cu-K_α radiation ($\lambda = 1.5418$ Å) was used for the collection of intensity data. Both structures were solved by direct methods (MULTAN [9]) and were refined by anisotropic full-matrix least-squares. Hydrogen atomic positions were calculated from assumed geometries. Though the generation of the hydrogen atomic positions of the *p*-tolyl methyl group is ambiguous, it is assumed not to have significant effect on the geometry of the relevant part of the molecule. No hydrogen atomic parameters were refined, but they were included in structure factor calculations. The isotropic temperature factors of the hydrogen atoms were fixed at $B(H) = B_{eq}(C) + 1$ Å^2, where $B_{eq}(C)$ is the equivalent isotropic temperature factor of the carbon atom to which the hydrogen atom is bonded. Empirical absorption corrections [10] were applied after the isotropic refinements of the non-hydrogen atoms (the minimum, maximum and average absorption corrections were as follows: I, 0.88, 1.43, 1.00; II, 0.75, 1.42, 1.02). Data collection and least-squares parameters are given in Table 1. Final atomic coordinates and equivalent isotropic temperature parameters are listed in Table 2 *.

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* Lists of hydrogen atomic coordinates, anisotropic temperature factors and observed and calculated structure factors may be obtained from the authors.

Discussion

Relevant bond distances and angles for I and II are shown in Table 3. The structure of the minor component of the stereoisomers of I was determined (Fig. 1). In this component the approximate three-fold symmetry is retained in the silatrane skeleton in contrast to the major component (e.g. p-tolyl-trimethyl-silatrane (III) [5]). The main conformational difference between I and III involves the conformation of the $\overline{\mathrm{Si{-}O{-}CH(CH_3){-}CH_2{-}N}}$ five membered rings. These rings are basically of envelope conformations. While atoms C(4), C(6) and C(11) (in α-position to the nitrogen atom) constitutes the flap of the envelope in I, C(3), C(7) and C(10) (β-positions) sits on the flap in III (Figs. 2 and 3). Further conformational difference is the positions of the "flap"-atoms with respect to the best plane formed by the remaining four atoms of the five-membered rings (C(3) and C(7) atoms lie on the same side of the planes, C(10) is on the opposite side; the methyl groups attached to C(3) and C(10) point to opposite directions in compound III).

The mean Si ← N distance (2.175(6) Å) is shorter by 0.061 Å in I than in III (2.236(3) Å). This is a rather unexpected result since there is no significant difference in the dative bond lengths in phenyl- and *p*-tolyl derivatives of unsubstituted or C-substituted silatranes or carbasilatranes (cf. Table 5.). The violation of the C_3 symmetry obviously results in unfavourable steric interactions.

There are slight conformational differences in the two independent molecules in the asymmetric unit of I. A least-squares fitting of the two silatrane moieties (with

Table 1

Unit cell, data collection and least-squares parameters

	I	II
Empirical formula	$C_{15}H_{23}NO_3Si$	$C_{14}H_{21}NO_2Si$
F.W. (a.m.u.)	293.44	263.41
$F(000)$	1264	2272
Crystal dimensions (mm)	0.15×0.30×0.35	0.30×0.40×0.50
a (Å)	11.086(1)	14.258(2)
b (Å)	17.145(2)	14.258(2)
c (Å)	16.910(2)	27.386(3)
β (°)	97.37(1)	
V (Å^3)	3188(1)	5567(2)
Space group	$P2_1/c$	$Pbca$
Z	8	16
D_x (g cm^{-3})	1.22	1.26
μ(Cu-K_α) (cm^{-1})	13.5	14.32
θ limits (°)	3–150	
Scan technique	θ–2θ	
No. of unique data	5500	4943
Reflections used in least-squares (NO) [a]	4221	3957
No. of variables (NV)	361	325
Weighting scheme (w)	$4F_o^2(\sigma(F_o^2))^2$	
R_{obs}	0.081	0.055
R_w	0.115	0.081
R_{tot}	0.102	0.072
$(\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO-NV))^{1/2}$	3.53	3.00

[a] $I > 3\sigma(I)$.

Table 2

Fractional coordinates and equivalent isotropic temperature factors (Å^2) with their ESDs. The atomic parameters for the second molecules are given in the second lines

Atom	x	y	z	B_{eq} ^{a}
Compound I				
Si(1)	0.71771(9)	0.70000(6)	0.53747(6)	3.53(3)
	0.22520(9)	0.58451(6)	0.19570(6)	3.67(3)
O(2)	0.6750(2)	0.7130(2)	0.6263(1)	5.2(1)
	0.2293(2)	0.6811(1)	0.1955(1)	4.6(1)
C(3)	0.7458(5)	0.6926(5)	0.6992(3)	9.7(3)
	0.3333(5)	0.7219(3)	0.1806(4)	10.1(3)
C(4)	0.8739(4)	0.6889(3)	0.6896(3)	6.7(2)
	0.4189(4)	0.6794(3)	0.1455(3)	6.6(2)
N(5)	0.8880(3)	0.6675(2)	0.6074(2)	4.7(1)
	0.4038(3)	0.5963(2)	0.1558(2)	4.3(1)
C(6)	0.9806(4)	0.7154(3)	0.5751(3)	6.5(2)
	0.3934(4)	0.5519(4)	0.0804(3)	6.7(2)
C(7)	0.9242(4)	0.7825(3)	0.5345(4)	7.9(2)
	0.2722(5)	0.5382(4)	0.0503(4)	10.0(3)
O(8)	0.8036(2)	0.7661(1)	0.5010(2)	5.5(1)
	0.1926(2)	0.5399(1)	0.1084(1)	5.1(1)
O(9)	0.7231(2)	0.6093(1)	0.5058(1)	4.7(1)
	0.3032(2)	0.5350(2)	0.2688(1)	5.7(1)
C(10)	0.8241(5)	0.5599(3)	0.5247(3)	7.9(2)
	0.4263(5)	0.5175(5)	0.2706(4)	15.6(3)
C(11)	0.8981(4)	0.5839(3)	0.5940(3)	6.2(2)
	0.4883(3)	0.5627(3)	0.2194(2)	4.8(1)
C(12)	0.7043(5)	0.7264(4)	0.7685(3)	7.5(2)
	0.3172(5)	0.8059(3)	0.1708(3)	6.7(2)
C(13)	0.9922(5)	0.8222(3)	0.4752(4)	7.9(2)
	0.2372(5)	0.4870(4)	−0.0156(3)	7.3(2)
C(14)	0.7949(4)	0.4787(2)	0.5107(3)	5.8(2)
	0.4851(4)	0.4915(3)	0.3494(3)	5.9(2)
C(15)	0.5680(3)	0.7295(2)	0.4788(2)	3.4(1)
	0.0713(3)	0.5726(2)	0.2320(2)	4.1(1)
C(16)	0.4649(3)	0.6831(2)	0.4750(2)	4.6(1)
	0.0354(4)	0.6209(3)	0.2895(2)	5.4(2)
C(17)	0.3539(4)	0.7065(2)	0.4370(3)	5.4(1)
	−0.0747(4)	0.6105(4)	0.3189(3)	7.6(2)
C(18)	0.3396(4)	0.7761(2)	0.3995(2)	5.1(1)
	−0.1505(4)	0.5526(4)	0.2913(3)	8.8(2)
C(19)	0.4393(4)	0.8245(2)	0.4013(2)	5.4(1)
	−0.1186(4)	0.5040(3)	0.2346(3)	8.2(2)
C(20)	0.5499(4)	0.8015(2)	0.4403(2)	4.7(1)
	−0.0086(4)	0.5146(3)	0.2048(3)	6.4(2)
Compound II				
Si(1)	0.65344(5)	0.59142(4)	0.10218(2)	2.95(2)
	0.33033(5)	0.15198(4)	0.14356(2)	3.15(2)
O(2)	0.5684(1)	0.5204(1)	0.12057(7)	4.20(8)
	0.4127(1)	0.0764(1)	0.12640(7)	4.75(9)
C(3)	0.5729(2)	0.4659(2)	0.1639(1)	5.0(1)
	0.4054(2)	0.0188(2)	0.0852(1)	6.3(1)
C(4)	0.6712(2)	0.4293(2)	0.1705(1)	4.9(1)
	0.3105(3)	0.0032(2)	0.0689(1)	8.1(2)
N(5)	0.7354(1)	0.5064(1)	0.16001(7)	3.67(9)
	0.2506(1)	0.0791(1)	0.08269(8)	4.2(1)

Table 2 (continued)

Atom	x	y	z	B_{eq} [a]
Compound II				
C(6)	0.8212(2)	0.4795(2)	0.1340(1)	4.4(1)
	0.1664(3)	0.0496(3)	0.1062(1)	10.1(2)
C(7)	0.7964(2)	0.4712(2)	0.0806(1)	4.5(1)
	0.1708(2)	0.0536(3)	0.1571(1)	8.2(2)
O(8)	0.7362(1)	0.5454(1)	0.06645(6)	3.97(7)
	0.2410(1)	0.1116(1)	0.17663(7)	4.96(9)
C(9)	0.6854(2)	0.6887(2)	0.1438(1)	4.2(1)
	0.3079(2)	0.2542(2)	0.10436(9)	4.3(1)
C(10)	0.7625(2)	0.6687(2)	0.1808(1)	4.8(1)
	0.2496(2)	0.2414(2)	0.0601(1)	6.4(1)
C(11)	0.7519(2)	0.5713(2)	0.2009(1)	4.9(1)
	0.2382(3)	0.1477(2)	0.0446(1)	9.1(2)
C(12)	0.5849(1)	0.6524(1)	0.05223(9)	3.2(1)
	0.3994(1)	0.2075(1)	0.19561(9)	3.4(1)
C(13)	0.5623(2)	0.6048(1)	0.0093(1)	3.7(1)
	0.4808(2)	0.1692(2)	0.2150(1)	4.7(1)
C(14)	0.5078(2)	0.6433(2)	−0.0270(1)	4.0(1)
	0.5315(2)	0.2131(2)	0.2513(1)	5.3(1)
C(15)	0.4725(2)	0.7334(2)	−0.0230(1)	4.0(1)
	0.5059(2)	0.2979(2)	0.2701(1)	4.6(1)
C(16)	0.4954(2)	0.7826(1)	0.0190(1)	4.3(1)
	0.4250(2)	0.3374(2)	0.2516(1)	4.9(1)
C(17)	0.5495(2)	0.7438(2)	0.0555(1)	3.9(1)
	0.3736(2)	0.2933(2)	0.2160(1)	4.4(1)
C(18)	0.4124(2)	0.7754(2)	−0.0626(15)	5.7(1)
	0.5625(2)	0.3467(3)	0.3087(1)	7.2(2)

[a] B_{eq} is defined as 4/3 trace **BG**, where **B** is the thermal motion tensor and **G** is the direct metric tensor.

the methyl groups included) of the asymmetric unit resulted in an r.m.s. deviation of 0.635 Å.

Least-squares lines through the N(5), Si(1), C(15) and C(18) atoms of both molecules of the asymmetric unit (the main molecular axes) form an angle of 55.2(1)°. Weak interactions exist between the π-system of the aryl ring and one of the hydrogen atoms of the methylene group in β-position to the nitrogen atom (the distance of the phenyl ring centroid of molecule 1 and H(4a′) [x, $1/2-y$, $1/2+z$] of molecule 2 is 2.83 Å; the distance of the phenyl ring centroid of molecule 2 and H(11b) [$\bar{x}$, $\bar{y}$, $\bar{z}$] of molecule 1 is 3.10 Å).

The relative orientation of the phenyl ring with respect to the silatrane moiety may be characterized by the smallest absolute value of the torsion angle O(X)–Si(1)–C(15)–C(16). For molecule 1 it is 46.9(6)° ($X=9$) and for molecule 2 38.9(6)° ($X=2$).

The Si ← N distance in the carbasilatrane II (Fig. 1) is 2.290(2) Å, in agreement with the value published for phenylcarbasilatrane (2.291(1) Å) [6]. The phenyl or p-tolyl substituents, therefore, do not differ in affecting the length of the Si ← N dative bond. The geometrical differences in the silatrane moiety of the two independent molecules are more pronounced in II (the r.m.s. deviation is 0.793 Å). The angle between the main molecular axes (N(5), Si(1), C(I12), C(15)) is identical with the value found for I (51.60(4)°). A weak interaction, similarly to compound I, is

Table 3

Relevant bond lengths (Å) and angles (°) with their ESDs. Second lines refer to the second molecules of the asymmetric unit

Bond lengths for compound I					
Si1-O2	1.648(3)	C3-C4	1.451(7)	C7-O8	1.412(6)
	1.657(3)		1.388(8)		1.403(7)
Si1-N5	2.167(3)	C3-C12	1.434(8)	C7-C13	1.495(9)
	2.182(3)		1.457(8)		1.432(10)
Si1-O8	1.650(3)	C4-N5	1.465(7)	O9-C10	1.409(6)
	1.661(3)		1.447(7)		1.394(6)
Si1-O9	1.647(3)	N5-C6	1.472(6)	C10-C11	1.403(8)
	1.650(3)		1.477(7)		1.407(9)
Si1-C15	1.890(4)	N5-C11	1.459(7)	C10-C14	1.442(8)
	1.897(4)		1.452(6)		1.474(9)
O2-C3	1.417(6)	C6-C7	1.441(9)		
	1.399(6)		1.394(8)		
Bond angles for compound I					
O2-Si1-N5	82.5(3)	O2-C3-C12	114.2(9)	C6-C7-C13	117.3(9)
	83.1(2)		115.0(9)		122.7(10)
O2-Si1-O8	119.6(3)	C4-C3-C12	122.1(10)	O8-C7-C13	110.7(8)
	117.5(3)		123.4(10)		115.1(9)
O2-Si1-O9	116.8(3)	C3-C4-N5	110.0(8)	Si1-O8-C7	123.3(6)
	120.2(3)		111.7(8)		123.2(6)
O2-Si1-C15	96.1(3)	Si1-N5-C4	105.2(5)	Si1-O9-C10	123.7(5)
	97.7(3)		104.6(5)		123.0(6)
N5-Si1-O8	82.9(3)	Si1-N5-C6	104.8(5)	O9-C10-C11	112.1(8)
	82.5(3)		104.2(5)		114.9(10)
N5-Si1-O9	82.5(2)	Si1-N5-C11	104.3(5)	O9-C10-C14	112.9(8)
	82.6(3)		105.0(4)		113.8(9)
N5-Si1-C15	178.6(3)	C4-N5-C6	112.1(7)	C11-C10-C14	121.0(9)
	178.8(3)		113.7(7)		121.9(10)
O8-Si1-O9	118.7(3)	C4-N5-C11	114.4(7)	N5-C11-C10	111.7(8)
	117.6(3)		113.9(6)		110.8(8)
O8-Si1-C15	97.5(3)	C6-N5-C11	114.8(7)	Si1-C15-C16	122.3(5)
	97.8(3)		114.0(6)		121.2(6)
O9-Si1-C15	98.5(3)	N5-C6-C7	109.9(8)	Si1-C15-C20	122.9(5)
	96.2(3)		111.5(9)		122.6(6)
Si1-O2-C3	124.6(6)	C6-C7-O8	111.3(8)	C16-C15-C20	114.6(6)
	121.6(6)		113.8(9)		116.2(7)
O2-C3-C4	110.7(9)				
	116.0(9)				
Bond lengths for compound II					
Si1-O2	1.658(2)	O2-C3	1.421(4)	C6-C7	1.508(4)
	1.662(2)		1.401(4)		1.395(6)
Si1-O8	1.668(2)	C3-C4	1.508(5)	C7-O8	1.416(4)
	1.666(2)		1.442(6)		1.403(5)
Si1-C9	1.852(3)	C4-N5	1.459(4)	C9-C10	1.521(4)
	1.838(3)		1.429(5)		1.482(5)
Si1-N5	2.311(2)	N5-C6	1.467(4)	C10-C11	1.502(4)
	2.269(3)		1.427(5)		1.411(5)
Si1-C12	1.892(3)	N5-C11	1.472(4)		
	1.905(3)		1.442(5)		

Table 3 (continued)

Bond angles for compound II					
O2–Si1–N5	80.9(2)	C9–Si1–C12	103.2(2)	C6–N5–C11	113.6(4)
	81.3(2)		101.4(2)		115.1(5)
O2–Si1–O8	117.1(2)	Si1–O2–C3	123.7(3)	N5–C6–C7	107.2(4)
	118.0(2)		123.8(4)		113.7(7)
O2–Si1–C9	116.7(2)	O2–C3–C4	109.4(4)	C6–C7–O8	110.5(4)
	118.1(2)		114.2(5)		115.9(6)
O2–Si1–C12	97.0(2)	C3–C4–N5	107.3(4)	Si1–O8–C7	124.2(3)
	96.6(2)		111.2(6)		122.8(4)
N5–Si1–O8	80.7(2)	Si1–N5–C4	102.3(3)	Si1–C9–C10	116.6(4)
	81.8(2)		104.4(4)		118.5(4)
N5–Si1–C9	81.1(2)	Si1–N5–C6	103.1(3)	C9–C10–C11	110.1(4)
	81.2(2)		103.0(4)		115.3(6)
N5–Si1–C12	175.6(2)	Si1–N5–C11	105.9(3)	N5–C11–C10	108.5(4)
	177.3(2)		106.4(4)		114.2(6)
O8–Si1–C9	118.8(2)	C4–N5–C6	114.9(4)	Si1–C12–C13	120.3(3)
	117.3(2)		113.5(5)		123.7(4)
O8–Si1–C12	97.0(2)	C4–N5–C11	115.1(4)	Si1–C12–C17	124.6(3)
	97.6(2)		113.3(5)		121.8(4)
				C13–C12–C17	115.0(4)
					114.4(4)

observed between the π-electron system of the aryl ring of molecule 2 and the H(9b) hydrogen atom of molecule 1 (the distance of H(9b) $[\bar{x}, 1/2+y, 1/2-z]$ from the phenyl ring centroid is 3.19 Å). The smallest absolute values of the torsion angles

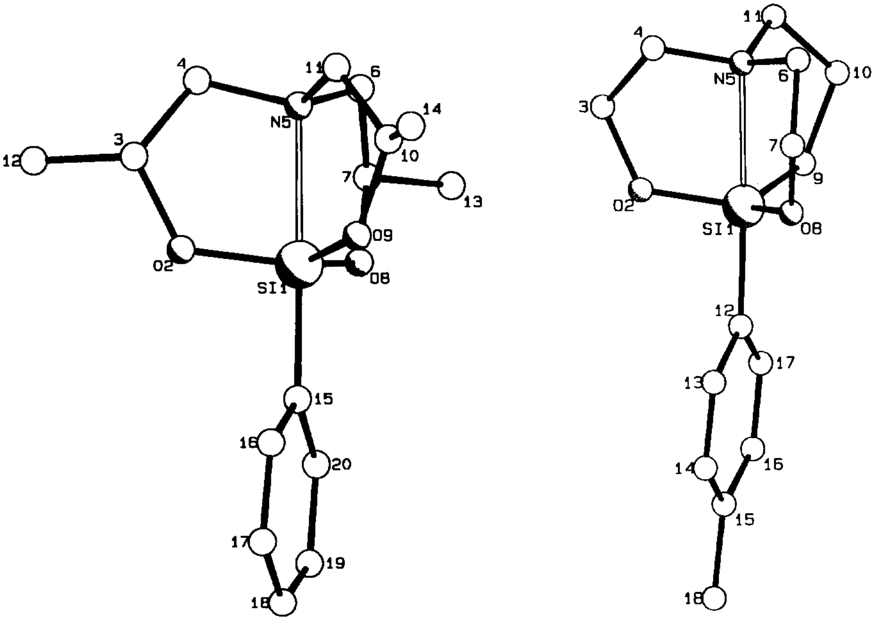

Fig. 1. The molecular diagrams of compounds I and II with the numbering of atoms. Only one molecule of the asymmetric unit is depicted. Hydrogen atoms are omitted for clarity.

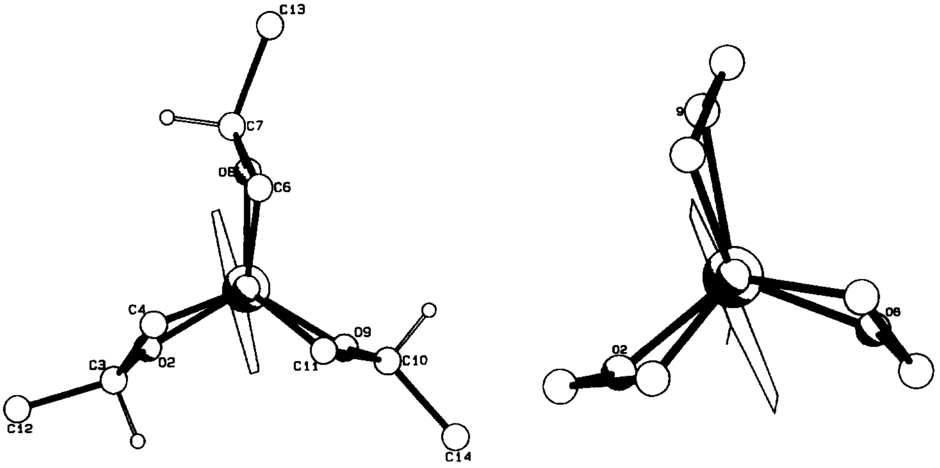

Fig. 2. Compounds I and II as viewed down the N–Si axis.

O(X)/C(3)–Si(1)–C(12)–C(13) are as follows: 47.0(4)° ($X = 8$, molecule 1) and 14.0° ($X = 2$, molecule 2). The small rotation of $\phi = 14°$ results in a rather short distance of 2.50 Å between atoms O(2′) ··· H(13′), similarly to phenyl-carbasilatrane ($\phi = 6°$; O(8) ··· H(13), 2.49 Å) [6].

The observed average ΔSi, ΔN, α(NSiO) and α(NSiC) values [1] for both structures agree with those predicted using structural correlations (Table 4).

The effect of the ring substitution on the molecular geometry of the silatrane, 3,7,10-trimethylsilatrane, carbasilatrane and silatranone series, is shown in Table 5. Within one series the Si ← N distances depend on the electron withdrawing/releasing nature of the apical substituent R. The shortest and the longest distances

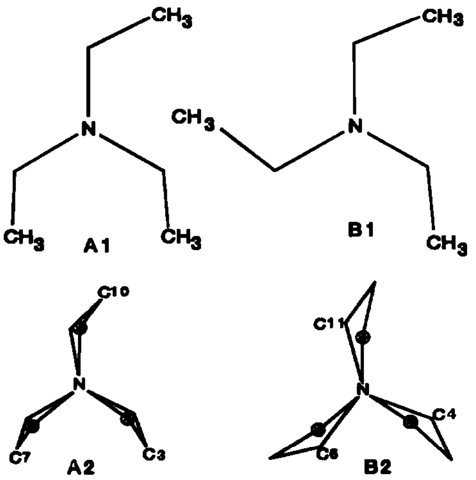

Fig. 3. Schematic representations of silatrane moieties. (A) Major stereoisomer fraction of 1-p-tolyl trimethylsilatrane; (B) minor stereoisomer fraction of I; relative positions of the methyl groups (A1, B1); the orientations of the "flap" atoms with respect to the remaining atoms of the conformational envelopes (A2, B2).

Table 4

Observed and calculated ΔSi, ΔN (Å), $\bar{\alpha}$(NSiO) (°) values

	Compound I		Compound II	
	Obs. [c]	Calc.	Obs. [c]	Calc.
ΔSi [a]	0.21	0.20	0.24	0.25
ΔN [b]	0.37	0.36	0.36	0.32
$\bar{\alpha}$(NSiO)	82.7	83.0	81.8	80.7

[a] The distance of the silicon atom from the plane of its equatorial substituents. [b] The distance of the nitrogen atom from the plane formed by its substituents. [c] Average values.

Table 5

Si ← N distances (Å) in various silatrane derivatives

R	$RSi(OCH_2CH_2)_3N$	$RSi[OCH(CH_3)CH_2]_3N$	$RSi(CH_2CH_2CH_2)(OCH_2CH_2)_2N$	$RSi(OCOCH_2)(OCH_2CH_2)_2N$
CH_3	2.175(4) [11]		2.336(4) [18]	2.134(1) [3]
C_6H_5 α	2.193(5) [12]	2.175(6) [a]	2.291(1) [6]	2.119(3) [2]
β	2.156(4) [13]			
γ	2.132(4) [14]			
p-$CH_3C_6H_4$	2.169(2) [5]	2.236(3) [5]	2.290(2) [a]	
$ClCH_2$	2.120(?) [15]	2.12(?) [17]		2.085(3) [19]
γ-$Cl(CH_2)_3$	2.181(?) [16]			2.149(5) [20]

[a] This work.

are observed in the chloromethyl- and the methyl derivatives, respectively. Comparing the geometry of the derivatives having identical R substituents at the silicon atom, it appears that the dative bond distance is longer by 0.12–0.16 Å in carbasilatranes, and it is shorter by 0.03–0.04 Å in silatranones with respect to silatranes. These differences may be explained by the electron density shifts caused by the substitutions O/CH_2 and $CH_2/C{=}O$ in the silatrane cage.

Trimethyl substitution, however, represents a more complex case, since the dative bond length seems to be different for the diastereomic species. The paper describing the structure of chloromethyl-trimethylsilatrane contains no information for the diastereomer present in the crystal: it is possible that the stereoisomers were not separated. The diastereomers might co-crystallize resulting in disordered crystal structures. All geometric data then refer to an average molecule. The cases of vinyltrimethylsilatrane and fluorotrimethylsilatrane [21] crystal structures are presumably identical to that of the chloromethyl derivative.

Acknowledgement

The financial support for this work by the Ministry of Education is gratefully acknowledged.

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