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SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE OF $O[Si(CH_2CH_2CH_2)_3N]_2$, AN OXYGEN-BRIDGED BIS(TRICARBASILATRANE)

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Summary

The hydrolysis of $ClSi(CH_2CH_2CH_2)_3N$ gives the compound $O[Si(CH_2CH_2CH_2)_3N]_2$ in high yield. Its structure has been investigated by ^1H, ^{13}C and ^{29}Si NMR spectroscopy and X-ray diffraction. The compound crystallizes in the cubic space group $Pa\bar{3}$. The unit cell with a 12.701(13) Å and V 2048.9 Å^3, contains four molecules. The structure was refined to a final R value of 0.092. The intramolecular Si–N distance is 2.477 Å. The silicon atoms have a distorted trigonal bipyramidal configuration.

Introduction

We have recently described the use of the trifunctional Grignard reagent $N(CH_2CH_2CH_2MgCl)_3$ as a suitable synthon for the preparation of a number of new tricarbametallatranes. $M(CH_2CH_2CH_2)_3N$ (M = RSi [1], RSn [2–4], P [5]). These derivatives can be directly compared with the stereochemical interesting manxine (M = CH) [6–8] and complete the family of metallatranes, which are of interest because of their unusual cage structures and their biological activity [9–13]. Originally we were interested in obtaining structural data for $ClSi(CH_2CH_2CH_2)_3N$ [1] for comparison with its tin analogue [3], but attempts to grow single crystals by slow evaporation of a concentrated solution of $ClSi(CH_2CH_2CH_2)_3N$ in methylene chloride/hexane yielded the disiloxane $O[Si(CH_2CH_2CH_2)_3N]_2$ (**1**) owing to the contact with atmospheric moisture. Thus we hydrolysed the $ClSi(CH_2CH_2CH_2)_3N$ under controlled conditions to give **1**, and determined its structure in solution and in the solid state.

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Experimental

The ^1H (200.13 MHz), ^{13}C (50.39 MHz) and ^{29}Si (39.76 MHz) NMR spectra were recorded on a Bruker WP 200 spectrometer with Me_4Si as external reference.

Synthesis of 1

Water (1 ml) was added to a solution of 3 g (14.7 mmol) of $ClSi(CH_2CH_2CH_2)_3N$ [1] in 20 ml triethylamine, and the mixture was stirred for 2 h, then 50 ml of benzene were added and the solvent was distilled off. The residue was extracted with methylene chloride and the extract washed twice with water to remove the triethylamine hydrochloride. After evaporation of the methylene chloride the residue was recrystallized from toluene at −20 °C to yield 2.3 g (89%) of colourless crystals, m.p. 228–230 °C. Analysis. Found: C, 61.28; H, 10.05; N, 7.83; $C_{18}H_{36}N_2OSi_2$ calc: C, 61.36; H, 10.23; N, 7.95%.

Crystal structure of 1

The space group and approximate cell dimension were derived from oscillation and Weissenberg photographs, then accurate unit cell dimensions were obtained by least-squares refinement of the angular positions of 15 reflections.

Crystal data. $C_{18}H_{36}ON_2Si_2$, $M = 352.67$; Cubic $Pa\bar{3}$, a 12.701(13) Å, V 2048.9(36) Å^3, $Z = 4$, D_{calc} 1.143 g cm^{-3}, $F(000) = 776$, μ 1.42 cm^{-1} (for Mo-K_α radiation). The intensities of 1419 reflections were measured on a Syntex P2_1 four-circle diffractometer, with graphite-monochromatized Mo-K_α radiation ($2\theta_{max}$ 47°). Of the 816 observed reflections with $I > 2.5\sigma(I)$, 355 unique data were used in the structure determination. The structure was solved by the heavy atom method and refined with the SHELX program (H atoms in calculated positions; non H atoms anisotropically; atom scattering factors included in program; weighting scheme = $|\sigma^2(F) + 0.0010\ F^2|^{-1}$) to a final conventional R value of 0.092. The final atomic coordinates are listed in Table 1. Tables of observed and calculated structure factors may be obtained from J.M.P. The maximum residual densities in the final difference Fourier map was 0.48 e Å^{-3}.

Results and discussion

The reaction of 1-aza-5-sila-chlorotricyclo [3.3.3.0^{1,5}] undecane with water in presence of triethylamine gives an almost quantitative yield of the title compound **1** (eq. 1).

TABLE 1

FRACTIONAL ATOMIC COORDINATES (×10^4) AND B_{eq} VALUES

Atom	x	y	z	B_{eq}
Si(1)	742(1)	742(1)	742(1)	3.74
N(1)	1867(4)	1867(4)	1867(4)	3.57
C(1)	2077(7)	585(7)	107(7)	6.37
C(2)	3014(6)	961(7)	671(8)	6.59
C(3)	2881(6)	1874(8)	1343(8)	6.71
O(1)	0(0)	0(0)	0(0)	8.03

TABLE 2

^1H, ^{13}C AND ^{29}Si NMR DATA OF COMPOUND **1** (in toluene-d_8; "t" pseudotriplet, "qu" pseudoquintet)

Nucleus	T (°C)	Chemical shifts (δ (ppm))		
		Si–CH_2	CH_2	NCH_2
^1H	25	0.68 ("t")	1.46 ("qu")	2.09 ("t")
	−85	0.91 [a]	1.49 [a]	1.93 [a]
^{13}C	25	15.91 [b]	23.93	54.19
	−85	15.80	23.70	53.50
^{29}Si	25	−18.40		

[a] Broad and unresolved. [b] $^1J(^{29}Si–^{13}C)$ 68.0 Hz.

$$2ClSi(CH_2CH_2CH_2)_3N + H_2O \xrightarrow[NEt_3\cdot HCl]{NEt_3} \underset{(\mathbf{1})}{O[Si(CH_2CH_2CH_2)_3N]_2} \qquad (1)$$

Compound **1** was obtained as colourless, sharp-melting crystals, which are soluble in polar organic solvents. Its NMR data are summarized in Table 2. At ambient temperature the ^1H NMR spectrum displays the expected well resolved patterns for the methylene protons, confirming that the concerted ring flip of the atrane frame is fast on the NMR time scale (Fig. 1). This means that we observe the average of the spectra of (**A**), (**A'**) ⇄ (**B**), and (**B'**). At −85°C all the methylene signals become broad and unresolved as the molecular interconversions shown in Fig. 1 are slowed

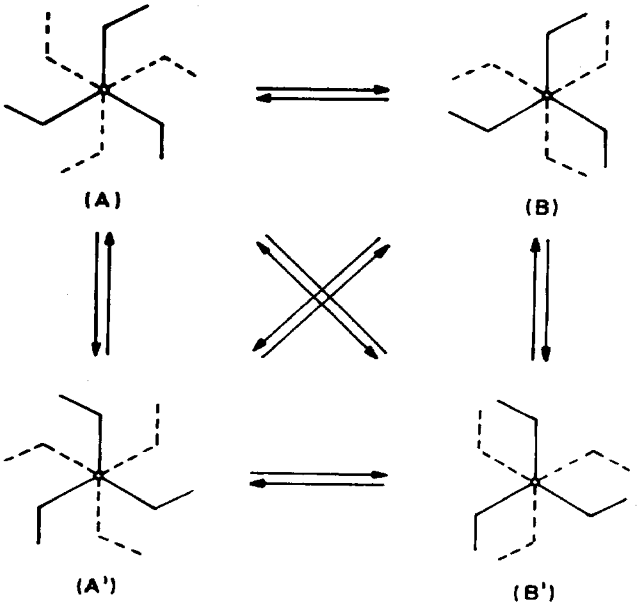

Fig. 1. Diastereomerisation (**A** ⇄ **B**, **A'** ⇄ **B'**) and enantiomerisation (**A** ⇄ **A'**, **B** ⇄ **B'**) processes of compound **1**.

down *. However, with NMR data available we cannot determine the ratios of the isomers (**A**), (**A′**) and (**B**), (**B′**) present in solution, or say whether both **A**- and **B**-type isomers are present at all. As discussed below only isomer (**A**)/(**A′**) is present in the solid state (Fig. 3).

The low field shift of the Si–CH_2 protons and the high field shift of the N–CH_2 protons at $-85\,°C$ may be attributed to a strengthening of the Si–N dative bond at this temperature. The ^{13}C NMR spectrum exhibits sharp signals for each carbon atom, with negligibly small changes in the δ values at low temperature. The $^{1}J(^{29}Si-^{13}C)$ coupling constant is greater than that for the tetrahedral species Me_3SiOMe (59.0 Hz) [14], and confirms the presence of a transannular donor–acceptor interaction. The ^{29}Si NMR signal is considerably shifted towards high field compared with that found for the signal from hexaethyl disiloxane (δ +9.11 ppm) [14].

Crystal and molecular structure

The molecular structure is illustrated in Fig 2, and a view along the N–Si–O axis is given in Fig. 3. Bond lengths and angles are listed in Table 3. The molecule belongs to the point group $\bar{3}$; the nitrogen and silicon atoms lie on the crystallographic three-fold axis and the O atom at the inversion centre. The Si–N distance is 2.477 Å, and lies at the upper limit for silicon–nitrogen interactions in silatranes [10]. Taking 1.823 Å as a standard Si–N bond length for pentacoordinated silicon [15] and 2.823 Å as the limit of non-bonding interaction, the value found in compound **1** reflects a formal bond order of only 0.35, illustrating the weak Lewis-acidity of the $OSiC_3$ skeleton. However, as is pointed out in ref. 15, estimated formal bond orders do not provide the best estimation of the position of a given structure along the pathway tetrahedron → trigonal bipyramid. A better approach is to take the difference between the sums of equatorial and apical angles [16], which is 0° in the case of an ideal tetrahedron and 90° in an ideal trigonal bipyramid. For compound **1** this difference is 40.2°, almost midway between the two geometries. The deviation of the silicon atom from the plane defined by the three adjacent carbon atoms is 0.399 Å; similar values have been found for other silatranes [10]. The nitrogen atom deviates by 0.364 Å from the plane of C(3), C(3)* and C(3)**. This value is in an usual range in such skeleton [3]. The torsion angles in the eight-membered rings listed in Table 4 correspond to a boat–chair conformation (the only one consistent with the molecular symmetry). Such a conformation has been found for $RSn(CH_2CH_2CH_2)_3N$ (R = Cl or Me) [3,4] and for 1-azabicyclo[3.3.0.]undecane hydrochloride [17]. A comparison of the torsion angles reveals that the conformation of the rings is rather similar to those for Sn-compounds [3,4]. The large value of the Si(1)–C(1)–C(2) angle (and also of the C(1)–C(2)–C(3) angle) is surprising, and could be the result of considerable ring strain. The two tricarbastannatranes which have been studied [3,4] do not show this angle expansion, whereas in manxine hydrochloride [17] the N–C–C and O–C–C bond angles are all substantially greater than tetrahedral.

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* The methyl signal of the toluene-d_8 remains sharp, confirming that there is adequate resolution at this temperature.

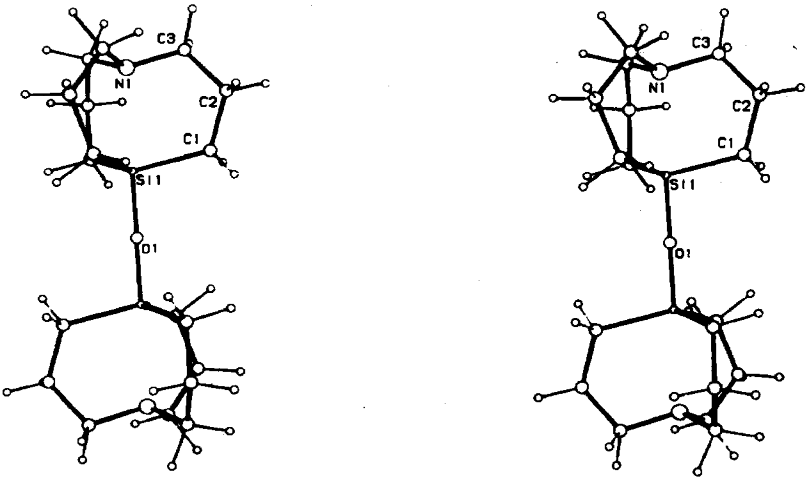

Fig. 2. Stereoscopic view of the molecular structure with atom numbering.

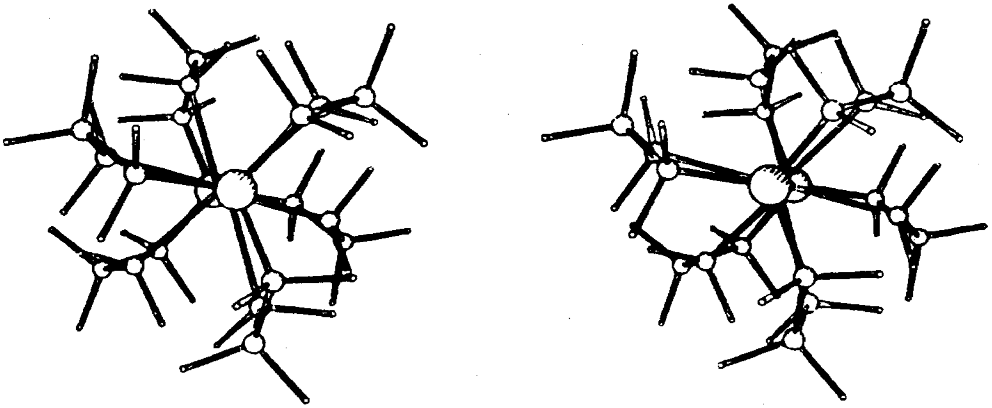

Fig. 3. Stereoscopic view along the N–Si–O axis.

TABLE 3

BOND LENGTHS (Å) AND BOND ANGLES (°)

Si(1)–O(1)	1.631(3)	C(1)–Si(1)–O(1)	102.2(3)
Si(1)–N(1)	2.477(5)	Si(1)–O(1)–Si(1)	180.0(0)
Si(1)–C(1)	1.888(8)	N(1)–Si(1)–O(1)	180.0(0)
C(1)–C(2)	1.469(12)	C(2)–C(1)–Si(1)	119.1(5)
C(2)–C(3)	1.449(12)	C(1)–Si(1)–C(1) [a]	115.6(2)
C(3)–N(1)	1.449(9)	C(1)–C(2)–C(3)	116.9(7)
		C(2)–C(3)–N(1)	111.7(7)
		C(3)–N(1)–C(3) [b]	113.9(4)

[a] Symmetry element z,x,y. [b] Symmetry element y,z,x.

TABLE 4

TORSION ANGLES IN THE EIGHT-MEMBERED RING

C(1)*–Si(1)–C(1)–C(2) = −57.4
Si(1)–C(1)–C(2)–C(3) = −32.2
C(1)–C(2)–C(3)–N(1) = +36.7
C(2)–C(3)–N(1)–C(3)* = +90.3
C(3)–N(1)–C(3)*–C(2)* = −136.6
N(1)–C(3)*–C(2)*–C(1)* = +36.7
C(3)*–C(2)*–C(1)*–Si(1) = −32.2
C(2)–C(1)–Si(1)–C(1) = +82.3

One of the well established features of trigonal bipyramidal molecules is the distinction between apical and equatorial bonds [18]: usually equatorial bonds are shorter than apical bonds as shown for many cases (e.g. ref. 4, 16, 18–21). However, there is no lengthening of the apical Si–O bond in compound **1** compared with those in some organo disiloxanes containing tetrahedral silicon (Si–O between 1.63 and 1.64 Å, [22–24]). The reasons for this could be the low polarizability of oxygen, and a somewhat disordered position of the oxygen; indeed, the six largest peaks of the final difference electron density are near the inversion centre (0.75 Å). An unexpected linear arrangement for Si–O–Si has been observed in other crystal structures [25–27], and Karle has revealed (Fig. 2 in [24]) a tendency toward a decrease in Si–O distance with increasing values of the Si–O–Si angle (in [25–27] Si–O between 1.61 and 1.62 Å).

Compound **1** is present in the crystal as discrete molecules, with no short intermolecular contacts.

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