THE CRYSTAL STRUCTURE
OF 1-*p*-CRESOXYSILATRANE,
$C_{13}H_{19}NO_4Si$

I. KOVÁCS, P. HENCSEI and L. PÁRKÁNYI*

Department of Inorganic Chemistry,
Technical University, H-1521 Budapest

Abstract

The crystal structure of 1-*p*-cresoxysilatrane (*p*-CH$_3$C$_6$H$_4$OSi(OCH$_2$CH$_2$)$_3$N) has been determined by *X*-ray diffraction. The Si$\leftarrow$N dative bond length is 2.107(2) $\mathring{A}$, which is 0.062 $\mathring{A}$ shorter than in the *p*-tolyl derivative because of the presence of apical oxigen atom.

Introduction

The five-coordinated silicon atoms in the 1-aryloxy derivatives of the silatrane series are surrounded by four oxygen atoms (three in equatorial—and one in apical position). The only known crystal structure of the 1-aryloxy silatrane derivatives is that of 1-m-chlorophenoxysilatrane [1] and we performed the structure determination of the title compound to throw light upon the effect of the phenyl ring substituent on the Si$\leftarrow$N dative bond.

The title compound was prepared by a published method [2].

Crystal data

Colourless transparent needles obtained from ethanol solution. $C_{13}H_{19}NO_4Si$, Fwt.: 281.4. a.m.u., m.p.: 196 $-$ 197 °C. $a = 8.999(1)$, $b = 10.822(2)$, $c = 7.283(1)$ $\mathring{A}$, $\beta = 107.16(1)^0$, $V = 677.7(3)$ $\mathring{A}^3$ (from single crystal diffractometry), monoclinic space group $P2_1$, $\mu(Cu - K_{\bar{\alpha}}, \lambda = 1.5418 \mathring{A})$ $= 16.2$ cm^{-1}, $D_c = 1.379$ gcm^{-3}.

* Central Research Institute of Chemistry of the Hungarian Academy of Sciences, Budapest-114, P.O.Box 17, H-1525, Hungary

Intensity data, structure determination and refinement

Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $Cu - K_{\alpha}$-radiation ($\theta - 2\theta$ scan, $1.5 \leq \theta \leq 75.0°$). 1484 unique intensities were measured of which 50 were recorded with zero intensity and these were excluded from the final data set after the determination of the structure. The approx. size of the crystal used was $0.10 \times 0.15 \times 0.25$ mm.

Several attempts to solve the structure with MULTAN [3] failed to give any reasonable structural fragments and finally, the random-phase generation procedure (with "RANTAN 10") gave all heavy atoms of the silatranyl group. The remaining atoms were located in a weighted Fourier map.

The structure was refined by anisotropic full-matrix least-squares for the non-hydrogen atoms. Hydrogen atoms were included in structure factor calculations in positions generated from assumed geometries. An empirical absorption correction [4] was applied at the end of the isotropic refinement (the maximum, minimum and average absorption corrections were 1.240, 0.800 and 0.971). The final R values are $R_0 = 0.035$, $R_w = 0.042$, $R_{tot} = 0.043$. A molecular diagram is depicted in Fig. 1., atomic parameters, bond distances and angles are given in Table 1 and 2.

Table 1

Atomic parameters for the non-hydrogen atoms ($\times 10^4$) and for the hydrogen atoms ($\times 10^3$) $B(eq)$ values are defined as $B(eq) = 4/3$ trace (B^*G) where B is the thermal motion tensor and G is the direct metric tensor

| Atom	x/a	y/b	z/c	B_{eq}	Atom	x/a	y/b	z/c	B
Si(1)	4068.5(8)	2773	4353(1)	2.84(1)	H(3a)	700	171	726	5.1
O(2)	5179(2)	2799(2)	6610(2)	3.46(5)	H(3b)	733	300	823	5.1
O(8)	3851(2)	4065(2)	3049(3)	3.68(6)	H(4a)	835	266	552	4.8
O(9)	3664(2)	1435(2)	3312(3)	3.34(6)	H(4b)	747	390	549	4.8
O(12)	2377(2)	3021(2)	4819(2)	3.50(6)	H(6a)	553	306	87	4.8
N(5)	6180(2)	2630(2)	3670(3)	3.14(6)	H(6b)	702	376	202	4.8
C(3)	6808(3)	2571(3)	7081(4)	4.1(1)	H(7a)	460	494	116	4.9
C(4)	7373(3)	3023(3)	5449(4)	3.8(1)	H(7b)	567	509	325	4.9
C(6)	6025(3)	3471(3)	2042(4)	3.8(1)	H(10a)	428	119	97	4.8
C(7)	5044(3)	4529(3)	2346(4)	3.9(1)	H(10b)	455	4	229	4.8
C(10)	4614(4)	913(3)	2266(5)	3.84(9)	H(11a)	673	85	433	4.8
C(11)	6276(3)	1317(3)	3195(5)	3.8(1)	H(11b)	688	122	233	4.8
C(13)	1767(3)	2307(3)	5977(4)	2.96(8)	H(14)	235	346	826	4.8
C(14)	1842(3)	2704(4)	7800(4)	3.79(8)	H(15)	125	233	1020	5.2
C(15)	1195(4)	2028(3)	8954(4)	4.2(1)	H(17)	−16	−23	603	5.0
C(16)	459(3)	911(3)	8338(4)	3.90(9)	H(18)	92	93	405	4.7
C(17)	356(3)	519(3)	6494(5)	4.0(0)	H(19a)	−66	−57	898	7.0
C(18)	1002(3)	1213(3)	5318(4)	3.66(9)	H(19b)	60	−6	1076	7.0
C(19)	−208(5)	155(4)	9633(6)	6.0(1)	H(19c)	−98	62	998	7.0
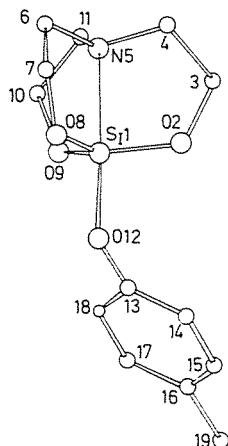
Fig. 1. A molecular diagram of 1-*p*-cresoxysilatrane with the numbering of atoms

Table 2

Bond lengths (Å) and bond angles (°) with their e.s.d.'s

Bond lengths

Si(1) — O(2)	1.653(2)	O(9) — C(10)	1.420(4)	C(10) — C(11)	1.513(4)
Si(1) — O(8)	1.669(2)	O(12) — C(13)	1.371(3)	C(13) — C(14)	1.378(4)
Si(1) — O(9)	1.625(2)	N(5) — C(4)	1.480(4)	C(13) — C(18)	1.383(5)
Si(1) — O(12)	1.677(2)	N(5) — C(6)	1.468(4)	C(14) — C(15)	1.367(5)
Si(1) — N(5)	2.107(2)	N(5) — C(11)	1.471(5)	C(15) — C(16)	1.388(5)
O(2) — C(3)	1.424(3)	C(3) — C(4)	1.506(4)	C(16) — C(17)	1.386(5)
O(8) — C(7)	1.411(3)	C(6) — C(7)	1.501(5)	C(16) — C(19)	1.501(5)
				C(17) — C(18)	1.389(5)

Bond angles

O(2) — Si(1) — O(8)	119.1(2)	C(4) — N(5) — C(11)	113.9(4)
O(2) — Si(1) — O(9)	117.7(2)	C(6) — N(5) — C(11)	114.0(4)
O(2) — Si(1) — O(12)	96.6(2)	O(2) — C(3) — C(4)	108.5(4)
O(2) — Si(1) — N(5)	85.0(2)	N(5) — C(4) — C(3)	105.7(4)
O(8) — Si(1) — O(9)	120.6(2)	N(5) — C(6) — C(7)	105.9(4)
O(8) — Si(1) — O(12)	91.2(2)	O(8) — C(7) — C(6)	109.0(5)
O(8) — Si(1) — N(5)	83.7(2)	O(9) — C(10) — C(11)	108.5(4)
O(9) — Si(1) — O(12)	98.3(2)	N(5) — C(11) — C(10)	105.4(4)
O(9) — Si(1) — N(5)	85.3(2)	O(12) — C(13) — C(14)	120.1(4)
O(12) — Si(1) — N(5)	174.7(2)	O(12) — C(13) — C(18)	121.2(4)
Si(1) — O(2) — C(3)	120.9(3)	C(14) — C(13) — C(18)	118.6(5)
Si(1) — O(8) — C(7)	122.0(3)	C(13) — C(14) — C(15)	121.1(5)
Si(1) — O(9) — C(10)	121.2(3)	C(14) — C(15) — C(16)	121.1(6)
Si(1) — O(12) — C(13)	125.9(3)	C(15) — C(16) — C(17)	118.0(5)
Si(1) — N(5) — C(4)	104.1(3)	C(15) — C(16) — C(19)	120.9(5)
Si(1) — N(5) — C(6)	105.5(3)	C(17) — C(16) — C(19)	121.2(5)
Si(1) — N(5) — C(11)	104.2(3)	C(16) — C(17) — C(18)	120.8(5)
C(4) — N(5) — C(6)	113.6(4)	C(13) — C(18) — C(17)	120.4(5)

Comments

The 2.107(2) $\overset{\circ}{A}$ value of the Si←N bond length corresponds to the electron-withdrawing property of the aryloxy substituent. This bond is longer by 0.062 $\overset{\circ}{A}$ in the p-tolyl derivative [5] because of the missing apical oxygen atom. The shorter Si←N bond in m-chlorophenoxysilatrane [1] (2.079(2) $\overset{\circ}{A}$)

Table 3

Observed and calculated geometric data for the title compound

$d(Si \leftarrow N), \overset{\circ}{A}$

Observed	Calculated	Correlation	Ref.
2.107(2)	2.151	$d = 3.021 \chi_R^{-0.257}$	[6]
	2.060	$d = 2.20 - 0.063\sigma_R^*$	[7]
	2.182	$\delta_{NCH_2} = 1.21\, d + 5.46$	[8]

$\Delta Si, \overset{\circ}{A}$ (see text)

Observed	Calculated	Correlation	Ref.
0.154	0.165	$\Delta Si = 0.488\, d - 0.863$	[6]
	0.166	$\Delta Si = 0.62\, d - 1.14$	[7]

$\Delta N, \overset{\circ}{A}$ (see text)

Observed	Calculated	Correlation	Ref.
0.372	0.390	$\Delta N = -0.391\, d + 1.214$	[6]

$O_{eq} - Si \leftarrow N(\alpha)$

Observed	Calculated	Correlation	Ref.
84.7 (mean)	84.4	$\alpha = -20.0\, d + 126.5$	[6]
	84.2	$\alpha = 120.9 - 17.4\, d$	[9]

may well be explained by the difference in the electron-withdrawing ability of the m-chloro and p-methyl substituents of the phenyl ring.

The dative bond length (d) in silatranes may be predicted by correlations utilizing the mean Sanderson electronegativity (X_R) and the inductive Taft constant (σ_R^*) of the R substituent on the silicon atom. The $^1H - NMR$ chemical shift of the $N - CH_2$ protons (δ_{NCH_2}), the configuration around the silicon and nitrogen atoms (i.e. distance of the silicon atom from the plane formed by the equatorial oxygens [ΔSi] and the distance of the nitrogen atom from the plane formed by its substituent carbon atoms [ΔN]) and the $O_{eq} - Si \leftarrow N$ angle were also shown to be correlated with d. These data (observed and calculated) are listed in Table 3.

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Ilona KOVÁCS
dr. Pál HENCSEI } H-1521 Budapest

dr. László PÁRKÁNYI H-1525 Budapest, POB 17