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THE CRYSTAL STRUCTURE OF 1-PHENYLCARBASILATRANE

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Summary

The crystal structure of 1-phenylcarbasilatrane, $[\mathrm{Ph\overset{\frown}{Si}(OCH_2CH_2)_2(CH_2CH_2CH_2)N}]$, has been determined by X-ray diffraction. The Si ← N dative bond length is 2.291(1) Å, which is 0.13 Å longer than the mean value found in the phenylsilatrane modifications. The conformation and the geometry of the carbasilatrane group is fairly similar to those of the silatrane moiety observed in normal silatranes.

Introduction

Carbasilatranes $[\mathrm{R\overset{\frown}{Si}(OCH_2CH_2)_2(CH_2CH_2CH_2)N}]$, 1-organyl-2,8-dioxa-5-aza-1-silatricyclo[3.3.3.$0^{1,5}$]undecanes, are a little studied class of silatrane-like, five-coordinated organosilicon compounds. They are derived formally from silatranes by substituting one equatorial oxygen atom with a CH_2 group. A few carbasilatranes are described in the literature and, to the best of our knowledge, only two (R = Me [1], and R = OMe [2]) crystal structure determinations have been performed so far.

Because of the missing equatorial oxygen atom, carbasilatranes have rather weak Si ← N bonds. The dative bond length in the methyl derivative [1] was found to be 0.161 Å longer than that in methylsilatrane [3]. The aim of the present study was to obtain geometrical data on the phenyl derivative to make further comparisons of the molecular structures.

Experimental

Synthesis

The compound 1-phenylcarbasilatrane was synthesized by a somewhat modified published method [4]. A xylene solution of phenyl(3-chloropropyl)dimethoxysilane was treated with diethanolamine in the presence of KOH as catalyst and triethyl-

TABLE 1

CRYSTAL DATA, DATA COLLECTION AND LEAST-SQUARES PARAMETERS

Empirical formula	$C_{13}H_{19}NO_2Si$
Mol. wt	249.4
Monoclinic:	
a (Å)	8.587(1)
b (Å)	12.078(1)
c (Å)	14.614(1)
β (deg.)	118.90(1)
V (Å^3)	1326.9(5)
Space group	$P2_1/c$
Z	4
$F(000)$	536
D_{calc}(gcm^{-3})	1.248
λ(Cu-K_α) (Å)	1.5418
μ(Cu-K_α) (cm^{-1})	14.8
2θ limits (deg.)	3–150
Scan technique	θ–2θ
Number of reflexions with non-zero intensity	2624
Number of reflexions used in least-squares	2477 $[F^2 > 3\sigma(F^2)]$
Number of variables	155
Weighting scheme	$w = 4IL/(\sigma(I)^2 + 0.01I^2))$ [a]
R_0	0.049
R_w	0.076
R_{tot}	0.051
S [b]	5.61

[a] Where I is the net intensity and L is the Lorenz-polarization factor. [b] For definition see ref. 6.

amine as HCl acceptor. The precipitated crude product was recrystallized from heptane. Yield 35%, m.p. 64–66°C (lit. 61–61.5°C).

Crystal structure analysis

Unit cell parameter determination and the collection of the intensity data was performed on a computer-controlled four-circle Enraf–Nonius CAD-4 diffractometer at room temperature using graphite-monochromated Cu-$K_{\bar{\alpha}}$ radiation. Crystal data, data collection and least-squares parameters are given in Table 1.

The structure was solved by direct methods and the non-hydrogen atomic parameters were refined by full-matrix least-squares. Hydrogen atom positions were generated from assumed geometries and were not refined. An empirical absorption correction [5] was applied. The maximum, minimum and the average absorption corrections were 0.842, 1.342 and 0.985. After absorption-correction non-hydrogen atoms were refined by anisotropic least-squares. The computer and computer programs used and the source of scattering factor data are given in ref. 6. Final positional parameters are listed in Tables 2 and 3 *.

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* Lists of structure-factor tables and anisotropic thermal parameters may be obtained from the authors on request.

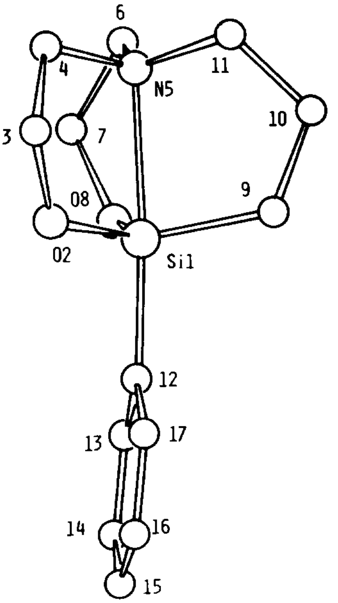

Fig. 1. The molecular diagram with atom numbering scheme for 1-phenylcarbasilatrane. The numbers refer to carbon atoms unless indicated otherwise. Hydrogen atoms are omitted for clarity.

Discussion

A molecular diagram is depicted in Fig. 1, bond lengths and bond angles are listed in Table 4.

TABLE 2

RELATIVE ATOMIC COORDINATES ($\times 10^4$) AND B_{eq} VALUES (Å^2) FOR THE NON-HYDROGEN ATOMS [a]

Atom	x/a	y/b	z/c	B_{eq}
Si(1)	1851.4(5)	2402.2(3)	3207.2(3)	2.464(8)
O(2)	1180(1)	1476(1)	3780.1(9)	2.93(2)
O(8)	605(1)	2628(1)	1938.3(9)	4.15(3)
N(5)	−387(1)	3401(1)	3243(1)	3.29(3)
C(3)	151(2)	1765(2)	4258(1)	3.69(5)
C(4)	−1251(2)	2590(2)	3585(1)	4.21(6)
C(6)	−1456(2)	3775(1)	2163(1)	4.42(4)
C(7)	−1203(3)	2951(2)	1477(1)	5.44(5)
C(9)	3216(2)	3572(1)	4056(1)	3.63(4)
C(10)	2184(3)	4615(1)	3979(1)	4.83(5)
C(11)	487(3)	4316(2)	3987(1)	4.44(5)
C(12)	3580(2)	1494(1)	3123(1)	2.68(3)
C(13)	3640(2)	1290(1)	2204(1)	3.61(4)
C(14)	4843(2)	570(2)	2159(1)	4.12(5)
C(15)	6068(2)	22(1)	3055(1)	3.80(4)
C(16)	6089(2)	228(1)	3974(1)	3.66(4)
C(17)	4874(2)	954(1)	4013(1)	3.05(3)

[a] B_{eq} is defined as in ref. 6.

TABLE 3

CALCULATED RELATIVE ATOMIC COORDINATES ($\times 10^3$) AND B VALUES ($Å^2$) FOR THE HYDROGEN ATOMS

Atom	x/a	y/b	z/c	B
H(3a)	−40	112	434	4.7
H(3b)	90	208	492	4.7
H(4a)	−173	294	398	5.2
H(4b)	−218	223	300	5.2
H(6a)	−107	449	208	5.4
H(6b)	−268	381	199	5.4
H(7a)	−155	328	81	6.4
H(7b)	−192	232	139	6.4
H(9a)	377	333	476	4.6
H(9b)	410	375	387	4.6
H(10a)	191	499	335	5.8
H(10b)	288	508	456	5.8
H(11a)	−28	494	379	5.4
H(11b)	75	409	467	5.4
H(13)	282	166	158	3.7
H(14)	484	45	151	3.7
H(15)	688	−49	303	3.7
H(16)	694	−13	459	3.7
H(17)	492	109	467	3.7

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) WITH THEIR e.s.d.s.

Bond lengths

Si(1)–O(2)	1.658(1)	O(8)–C(7)	1.416(2)	C(9)–C(10)	1.513(3)
Si(1)–O(8)	1.655(1)	N(5)–C(4)	1.455(2)	C(10)–C(11)	1.507(2)
Si(1)–N(5)	2.291(1)	N(5)–C(6)	1.463(3)	C(12)–C(13)	1.390(2)
Si(1)–C(9)	1.871(2)	N(5)–C(11)	1.476(3)	C(12)–C(17)	1.398(2)
Si(1)–C(12)	1.897(1)	C(3)–C(4)	1.505(3)	C(13)–C(14)	1.377(3)
O(2)–C(3)	1.409(2)	C(6)–C(7)	1.500(3)	C(14)–C(15)	1.388(3)
				C(15)–C(16)	1.357(3)
				C(16)–C(17)	1.386(2)

Bond angles

O(2)–Si(1)–O(8)	118.8(1)	C(4)–N(5)–C(11)	114.4(3)
O(2)–Si(1)–N(5)	81.0(1)	C(6)–N(5)–C(11)	113.2(3)
O(2)–Si(1)–C(9)	115.7(1)	O(2)–C(3)–C(4)	109.6(3)
O(2)–Si(1)–C(12)	96.7(1)	N(5)–C(4)–C(3)	106.9(3)
O(8)–Si(1)–N(5)	81.0(1)	N(5)–C(6)–C(7)	107.4(3)
O(8)–Si(1)–C(9)	118.5(1)	O(8)–C(7)–C(6)	110.1(3)
O(8)–Si(1)–C(12)	97.2(1)	Si(1)–C(9)–C(10)	115.0(2)
N(5)–Si(1)–C(9)	81.4(1)	C(9)–C(10)–C(11)	109.5(3)
N(5)–Si(1)–C(12)	175.8(1)	N(5)–C(11)–C(10)	108.8(3)
C(9)–Si(1)–C(12)	102.8(1)	Si(1)–C(12)–C(13)	124.1(2)
Si(1)–O(2)–C(3)	122.5(2)	Si(1)–C(12)–C(17)	120.2(2)
Si(1)–O(8)–C(7)	123.0(2)	C(13)–C(12)–C(17)	115.6(2)
Si(1)–N(5)–C(4)	103.1(2)	C(12)–C(13)–C(14)	122.5(3)
Si(1)–N(5)–C(6)	103.5(2)	C(13)–C(14)–C(15)	120.0(3)
Si(1)–N(5)–C(11)	106.1(2)	C(14)–C(15)–C(16)	119.2(3)
C(4)–N(5)–C(6)	114.8(3)	C(15)–C(16)–C(17)	120.5(3)
		C(12)–C(17)–C(16)	122.1(3)

TABLE 5

SOME CHARACTERISTIC GEOMETRICAL DATA FOR CARBASILATRANES AND PHENYLSILATRANES

R	$RSi(OCH_2CH_2)_2(CH_2CH_2CH_2)N$			$RSi(OCH_2CH_2)_3N$		
	C_6H_5	CH_3 [1]	CH_3O [2]	α-C_6H_5 [7]	β-C_6H_5 [8]	γ-C_6H_5 [9]
Si ← N (Å)	2.291(1)	2.336(4)	2.223(5)	2.193(5)	2.156(4)	2.132(4)
Si–CH_2 (Å)	1.871(2)	1.898(5)	1.848(6)	–	–	–
Si–O(mean) (Å)	1.657(2)	1.666(3)	1.656(4)	1.656(8)	1.657(2)	1.656(2)
Si–R (Å)	1.897(1)	1.877(5)	1.671(4)	1.882(6)	1.908(5)	1.894(5)
NSiR (°)	175.8(1)	176.8(2)	178.8(5)	177.9(2)	177.0(3)	179.0(2)
$NSiX_{eq}$(mean) (°)	81.1(2)	80.1(1)	82.4(2)	82.9(2)	83.3(5)	83.7(2)
ΔSi (Å)	0.27	0.29	0.23	0.20	0.20	0.18
ΔN (Å)	0.36	0.35	0.37	0.34	0.38	0.39

Si ← N bond length data for carbasilatranes indicate reduced partial positive charge on silicon (reduced acceptor ability). The dative bond lengths are as follows: in methylcarbasilatrane 2.336(4) [1], in methylsilatrane 2.175(4) [3], in 1-phenylcarbasilatrane 2.291(1);, in phenylsilatrane modifications 2.193(5), 2.156(4), and 2.132(4) Å [7–9].

Other features of the molecular geometry conform to those of normal silatranes (cf. Table 5) showing that the equatorial methylene group only slightly affects the silatrane skeleton. The lack of three-fold symmetry somewhat deforms the NSiR angles, a 4° deviation from 180° is observed in the title compound. Correlations established between the Si ← N distances and some characteristic features of the silatrane moiety [10–12] are also valid for the carbasilatrane series. These data, the average $NSiX_{eq}$ angle, the distance of the silicon atom from the plane of its equatorial substituents, ΔSi, and the distance of the nitrogen atom from the plane of its substituents, ΔN, are also listed in Table 5.

A comparison of the dative bond lengths observed in carbasilatranes also indicates that the electron-withdrawing property of R is an important factor in the donor–acceptor interaction. The phenyl group having a more electron-withdrawing nature than methyl, a shorter dative bond is formed in the title compound. An electron-withdrawing OMe substituent results in a shorter, 2.223(4) Å, Si ← N bond. This value is, however, still longer than that observed in methylsilatrane, indicating that an oxygen atom in the apical position has less effect on the acceptor ability of silicon than one in the equatorial position.

The relative position of the phenyl ring with respect to the carbasilatrane moiety can be characterized by the rotation about the Si(1)–C(12) bond. The O(8)–Si(1)–C(12)–C(13) torsion angle is small, 6.0(2)°, thus, H(13) forms a rather short contact with O(8), 2.49 Å.

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