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Crystal and molecular structure of 1-phenyl-2,8,9-triazasilatrane

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Abstract

The crystal and molecular structure of 1-phenyl-2,8,9-triazasilatrane $\overline{N(CH_2CH_2NH)_3Si}Ph$ has been established by an X-ray structural study. The Si atom has a somewhat distorted trigonal bipyramidal penta-coordination (typical of atranes) with three N atoms in the equatorial positions and N and C(Ph) atoms in the axial positions. The transannular N→Si bond length is 2.132(4) Å. The exchange of equatorial O atoms with N atoms, i.e. a transition from silatrane to triazasilatrane, causes no significant changes in the structure of the atrane framework.

Introduction

2,8,9-Triazasilatranes $\overline{N(CH_2CH_2NH)_3Si}R$ (I) in contrast to the usual silatranes $\overline{N(CH_2CH_2O)_3Si}R$ (II) have some unique features because of the presence of the less-polar NH groups relative to oxygen, in particular I have much smaller observed dipole moments [1,2]. On the other hand, NMR studies [3,4] indicate a stronger donor–acceptor N→Si interaction in triazasilatranes (I) than in the silatranes (II).

In order to elucidate the geometrical differences of triazasilatrane molecules we carried out an X-ray study on 1-phenyl-2,8,9-triazasilatrane (Ia, R = Ph).

Experimental

1-Phenyl-2,8,9-triazasilatrane was prepared by a standard procedure [1], viz. by heating a mixture of tris(2-aminoethyl)amine and phenyltris(dimethylamino)silane without solvent. Colorless crystals of Ia (m.p. 90–93°C) were obtained after crystallization from chloroform.

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Table 1

Atomic coordinates (for Si, N, C $\times 10^4$; for H $\times 10^3$) and thermal parameters

Atom	*x*	*y*	*z*	B_{eq} (Å^2)	Atom	*x*	*y*	*z*	B_{ios} (Å^2)
Si	1786(2)	1135(1)	3251(1)	1.44(3)	H(N2)	33(5)	214(3)	415(3)	3(1)
N(1)	−153(5)	133(3)	2601(3)	1.59(9)	H(N3)	359(4)	−14(3)	393(3)	0.8(8)
N(2)	66(5)	1815(3)	3758(3)	2.0(1)	H(N4)	319(4)	165(3)	184(3)	0.9(8)
N(3)	2418(4)	−127(3)	3798(3)	1.9(1)	H(1.1)	−264(4)	197(3)	367(3)	0.5(8)
N(4)	2275(4)	1340(3)	1970(3)	1.8(1)	H(1.2)	−201(4)	89(3)	422(3)	1.7(9)
C(1)	−1639(6)	1417(4)	3672(4)	2.0(1)	H(2.1)	−189(5)	121(4)	219(4)	3(1)
C(2)	−1732(5)	779(4)	2669(4)	1.9(1)	H(2.2)	−298(5)	31(4)	262(3)	3(1)
C(3)	1589(6)	−1163(4)	3515(4)	2.0(1)	H(3.1)	172(5)	−167(4)	412(3)	3(1)
C(4)	−193(6)	−887(4)	3231(4)	2.0(1)	H(3.2)	241(6)	−155(4)	289(4)	5(1)
C(5)	1215(6)	958(4)	1132(4)	2.3(1)	H(4.1)	−81(4)	−70(3)	392(3)	1.2(9)
C(6)	328(6)	−94(4)	1520(4)	1.9(1)	H(4.2)	−97(5)	−138(3)	295(3)	1.8(9)
C(7)	3460(5)	2075(4)	3863(4)	1.8(1)	H(5.1)	210(6)	79(4)	51(4)	6(2)
C(8)	4051(5)	3054(4)	3392(4)	1.8(1)	H(5.2)	25(4)	141(3)	88(3)	1.4(9)
C(9)	5145(6)	3770(4)	3877(4)	2.3(1)	H(6.1)	130(4)	−73(3)	157(3)	1.3(9)
C(10)	5691(6)	3561(4)	4864(4)	2.4(1)	H(6.2)	−86(5)	−21(3)	104(3)	2(1)
C(11)	5144(6)	2609(4)	5359(4)	2.1(1)	H(8)	369(5)	323(3)	275(3)	2(1)
C(12)	4049(6)	1899(4)	4862(4)	1.9(1)	H(9)	−564(5)	−58(4)	150(4)	3(1)
					H(10)	−651(5)	−109(4)	−14(3)	2.2(9)
					H(11)	555(5)	241(4)	607(3)	3(1)
					H(12)	366(4)	134(3)	518(3)	1.5(9)

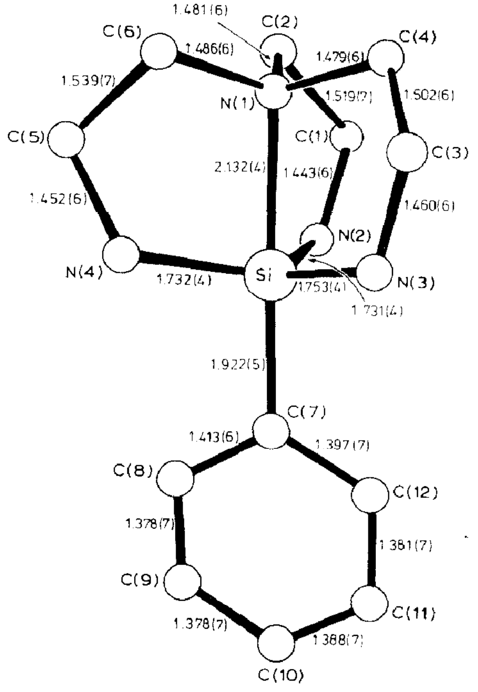


Fig. 1. The structure of 1-phenyl-2,8,9-triazasilatrane (Ia) showing bond lengths.

Table 2

Bond angles (deg.)

N(1)SiN(2)	81.3(2)	SiN(1)C(4)	105.6(3)	N(1)C(4)C(3)	107.4(4)
N(1)SiN(3)	82.9(2)	SiN(1)C(6)	106.9(3)	N(4)C(5)C(6)	106.3(4)
N(1)SiN(4)	82.2(2)	C(2)N(1)C(4)	112.7(3)	N(1)C(6)C(5)	106.2(4)
N(1)SiC(7)	177.5(2)	C(2)N(1)C(6)	112.0(3)	SiC(7)C(8)	123.1(3)
N(2)SiN(3)	118.9(2)	C(4)N(1)C(6)	112.2(3)	SiC(7)C(12)	121.7(3)
N(2)SiN(4)	118.7(2)	SiN(2)C(1)	123.9(3)	C(8)C(7)C(12)	114.9(4)
N(2)SiC(7)	96.2(2)	SiN(3)C(3)	120.8(3)	C(7)C(8)C(9)	122.4(4)
N(3)SiN(4)	116.8(2)	SiN(4)C(5)	123.1(3)	C(8)C(9)C(10)	120.6(4)
N(3)SiC(7)	98.5(2)	N(2)C(1)C(2)	106.1(4)	C(9)C(10)C(11)	119.1(4)
N(4)SiC(7)	99.0(2)	N(1)C(2)C(1)	106.2(4)	C(10)C(11)C(12)	119.6(4)
SiN(1)C(2)	106.9(3)	N(3)C(3)C(4)	107.3(4)	C(7)C(12)C(11)	123.4(4)

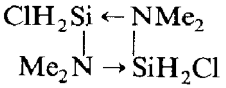
Crystals of Ia ($C_{12}H_{20}N_4Si$) are monoclinic with a 7.958(3), b 12.069(6), c 13.024(7) Å, β 90.22(4)°, V 1250(1) Å^3, d_{calc} 1.319 g cm^{-3}, $Z=4$, space group $P2_1/c$. The cell parameters and intensities of 2758 independent reflections were measured with a Syntex P2$_1$ four-circle automatic diffractometer at −120 °C (Mo-K_α radiation, θ–2θ scan, θ_{max} 30°). The structure was solved by direct methods by use of the MULTAN program and refined by block-diagonal least-squares procedure in an anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were localized in the difference map and refined isotropically. Final values of discrepancy factors are $R=0.059$ and $R_w=0.060$ for 1858 reflections with $I \geqslant 2\sigma(I)$. All calculations were performed by an Eclipse S/200 computer using the INEXTL program [4]. The atomic coordinates and thermal parameters are listed in Table 1, the structure and bond lengths are shown in Fig. 1, bond angles are given in Table 2.

Results and discussion

The silicon atom in the crystal of triazasilatrane Ia has a somewhat distorted trigonal bipyramidal coordination, with three N atoms in the equatorial positions and N and C(Ph) atoms in the axial positions which are typical atrane features. The transannular N→Si bond length of 2.132(4) Å agrees with that found in the γ-modification of 1-phenylsilatrane (γ-IIa, R = Ph) [5] and is somewhat shorter than in the two other (α and β) modifications of IIa, viz. 2.193(5) [6] and 2.156(4) Å [7]. At the same time the Si–C(Ph) bond length of 1.922(5) Å in Ia is greater than that in α-, β- or γ-IIa (1.882(6), 1.908(4) and 1.894(5) Å, respectively). The NSiC bond angle formed by the axial substituents in triazasilatrane Ia is 177.5(2)° very close to the values in 1-phenylsilatrane (177.9, 177.0 and 179.0° in α-, β- and γ-IIa, respectively). The deviation of silicon atom from the plane of three equatorial N atoms toward the C(7) atom in Ia (0.239(1)Å) is somewhat greater than the analogous deviation in γ-IIa (0.183Å). This difference, along with the approximately similar N→Si distances in both molecules, causes a greater deviation by the axial N atom from the plane of the three N-bonded C atoms toward the Si atom in Ia (0.420(4) Å) than in γ-IIa (0.395 Å).

The equatorial N–Si bond lengths in Ia (1.731(4)–1.754(4) Å, average 1.739 Å) are somewhat greater than the N–Si distances in the tetrahedral silicon derivatives (e.g. 1.715(4) Å in H_3SiNMe_2 [8]) and are very close to the equatorial N–Si bond lengths (1.746(2) Å) at the pentacoordinated Si atom in the molecule of 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline [9]. This feature of Ia is in line with the increase in equatorial Si–O bond lengths (e.g., 1.656, 1.657 and 1.656 Å in α-, β- and γ-IIa) which is characteristic for silatranes, with Si–O distances in tetrahedral silicon derivatives (1.61–1.63 Å, cf. for instance [10]).

The N(1)–C bond lengths (1.479–1.486(6) Å) in the crystalline Ia are greater than the N–C bond lengths (1.443–1.460(6) Å) in tri-coordinated equatorial nitrogen atoms, and such an increase is usual for the transition of nitrogen atom from tri- to tetra-coordination. For the transition from monomeric $ClH_2Si–NMe_2$ (gas) to its dimeric form:



$$\begin{array}{l} ClH_2Si \leftarrow NMe_2 \\ \quad\;\; | \qquad\;\; | \\ \;Me_2N \rightarrow SiH_2Cl \end{array}$$

(crystal) an increase of the N–C distance from 1.464(4) to 1.498(18) Å is observed [11].

The five-membered chelate heterocycles in triazasilatrane Ia, like those in the silatranes with unsubstituted chelate cycles, have the envelope conformation with deviations of the α-carbon atoms from the plane of the four other atoms in the cycle of 0.530(5), 0.535(5) and 0.526(5) Å for C(2), C(4) and C(6), respectively.

In general, the triazasilatrane framework of Ia is in accord with C_3 symmetry, and is distorted only by the presence of the Ph substituent.

The dihedral angles between the phenyl ring and the planes of four coplanar atoms in chelate cycles of the triazasilatrane framework are 94.8, 35.5 and 27.4° for the fragments N(I)SiN(2)C(I), N(I)SiN(3)C(3) and N(I)SiN(4)C(5), respectively. This conformation of Ia results in short non-bonded contacts between the equatorial N atoms of triazasilatrane framework and the phenyl ring atoms: N(3)...C(12) 3.093(6) and N(4)...C(8) 3.112(6) Å (the sum of the Van der Waals radii of N and C atoms being 3.25 Å [12]). The N(2) atom has no short contacts with the phenyl ring.

The C(8)C(7)C(12) bond angle at the *ipso*-carbon of phenyl ring in Ia is decreased to 114.9(4)°, which is typical of Ph derivatives with electron-donating substituents [13]. The corresponding angle in γ-IIa is 116.6(5)° and that in the tetrahedral bis(triphenylsilyl)silicon oxide derivative is 116.7° (average) [14].

Thus, replacement of equatorial oxygen atoms in the silatrane by nitrogen atoms in the triazasilatrane causes no significant changes in the structure of the atrane framework and in particular, in the trigonalbipyramidal geometry of the silicon atom.

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