

THE CRYSTAL STRUCTURE OF 1-*m*-CHLOROPHENOXY-SILATRANE

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(Received January 19th, 1982)

Summary

The pentavalent silicon in the title compound is coordinated by four oxygen atoms. The N→Si dative bond is rather short (2.079(2) Å). The crystal structure is partially disordered: carbon atoms attached to nitrogen appear on both sides of the Si—O(eq)—C, N plane with a population of 0.8 and 0.2, respectively. The change of the configuration around silicon and nitrogen, as a function of the N→Si dative bond length, is reviewed for several silatrane structures. Structural data suggest that different extents of the distortion of the trigonal bipyramid around silicon for the various compounds may represent stages along the pathway of the S_N2 -type reaction $\equiv\text{Si}-\text{X} + \text{HN}\equiv \rightarrow \equiv\text{Si}-\text{N}\equiv$.

Introduction

The crystal structure of 1-*m*-chlorophenoxy-silatrane is of special interest because the pentavalent silicon is coordinated by four oxygen atoms; three of them in equatorial positions and one in an apical position. Because of the electron-withdrawing nature of the *m*-chlorophenoxy substituent the N→Si dative bond was also expected to be short [1].

Experimental

1-*m*-Chlorophenoxy-silatrane was prepared as described by Voronkov et al. [2]. Yield: 57.0%. Anal. Found: C, 47.45; H, 5.44; N, 4.66; Si, 9.30; $\text{C}_{12}\text{H}_{16}\text{ClNO}_4\text{Si}$ calcd.: C, 47.76; H, 5.34; N, 4.64; Si, 9.31%. M.p. 243–245°C. ^1H -NMR data (ppm/TMS): 3.90 t (OCH₂); 2.92 t (NCH₂).

Data collection, the determination and refinement of the structure

Crystal data: $C_{12}H_{16}O_4NSiCl$, Fwt.: 301.8, a 11.406(1), b 8.017(2), c 14.455(1) Å, β 97.20(2)°, V 1311.4(6) Å³, space group $P2_1/c$, $Z = 4$, ρ_x 1.529 Mg m⁻³, $F(000)$ 632, $\mu(Mo-K\alpha, \lambda 0.7107 \text{ \AA})$ 0.39 mm⁻¹.

3147 independent intensities were measured on an Enraf-Nonius CAD 4 four-circle computer controlled diffractometer with graphite monochromated Mo- $K\alpha$ radiation with $\theta-2\theta$ scan ($3 \leq 2\theta \leq 50^\circ$).

The approx. size of the crystal was 0.11 × 0.25 × 0.35 mm. 579 reflexions were recorded with zero intensity and after the determination of the structure, these were excluded from the final data set.

The structure was determined by direct methods using the MULTAN program [3]. 2382 reflexions [$F_0 \geq 3\sigma(F_0)$] were used in full-matrix least-squares refinement. The weighting scheme applied was: $w = 4F^2/\sigma(F^2)^2$; (where $\sigma(F_0^2)^2 = [\sigma(I)^2 + (0.01 I)^2]^{1/2}/Lp$; Lp is the Lorenz-polarization factor and I is the net intensity). An ordered structure with calculated hydrogen atomic positions was refined to $R = 0.060$. A difference map, calculated at this stage, clearly revealed that the carbon atoms attached to the N(5) atom are disordered. Three additional atoms assigned as carbons were also included in the calculations. The multiplicities of the disordered atoms were then refined with their sum fixed at 3.0. The multiplicities refined to 0.80 and 0.20, respectively, for each disordered atom-pairs. Hydrogen atoms in assumed positions were also added to the disordered carbon atoms with the corresponding multiplicities. The final R was 0.041 ($R_w = 0.052$) for observed and 0.067 for all (2531) reflexions. No absorption correction was made. Atomic scattering factors were

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND $B(\text{eq})$ VALUES FOR THE NON-HYDROGEN ATOMS. $B(\text{eq})$ is defined as $4(b_1^2 b_2^2 b_3^2 / a^2 b^2 c^2)^{1/3}$

Atom	x/a	y/b	z/c	$B(\text{eq}) (\text{\AA}^2)$
Si(1)	7947(1)	1141(1)	3086(1)	1.97(1)
O(2)	6558(2)	611(2)	2714(1)	2.55(3)
C(3)	5802(3)	1692(4)	2134(2)	3.3(1)
C(4)	6239(3)	3456(5)	2235(3)	3.1(1)
C(4')	6555(12)	3029(19)	1655(10)	3.7(3)
N(5)	7553(2)	3353(3)	2363(2)	2.40(4)
C(6)	8156(4)	4676(5)	2941(3)	3.6(1)
C(6')	7377(16)	4648(19)	3100(9)	3.6(3)
C(7)	8070(3)	4097(4)	3967(2)	3.6(1)
O(8)	8202(2)	2340(2)	4022(1)	2.93(4)
O(9)	8970(2)	902(2)	2386(1)	2.94(3)
C(10)	9142(3)	2102(4)	1687(2)	3.5(1)
C(11)	8016(3)	3144(5)	1450(2)	3.3(1)
C(11')	8658(11)	3831(17)	1982(11)	2.9(2)
O(12)	8340(2)	-671(2)	3638(1)	2.73(3)
C(13)	7988(2)	-1324(3)	4420(2)	2.22(4)
C(14)	6799(2)	-1493(4)	4533(2)	2.7(1)
C(15)	6507(3)	-2256(4)	5330(2)	3.0(1)
C(16)	7335(3)	-2856(4)	6025(2)	3.0(1)
C(17)	8520(3)	-2666(4)	5909(2)	3.1(1)
C(18)	8852(2)	-1909(4)	5118(2)	2.7(1)
Cl	5010(1)	-2427(1)	5470(1)	4.87(2)

TABLE 2

ATOMIC COORDINATES ($\times 10^3$), B VALUES AND C—H DISTANCES FOR THE HYDROGEN ATOMS

Atom	x/a	y/b	z/c	B (\AA^2)	C—H (\AA)
H(3a)	505	173	239	4.0	0.98
H(3b)	570	126	151	4.0	0.96
H(4a)	594	414	168	4.2	0.99
H(4b)	596	399	281	4.2	1.02
H(4a)'	605	409	158	4.6	1.03
H(4b)'	676	264	109	4.6	0.93
H(6a)	899	478	284	4.7	0.98
H(6b)	774	576	283	4.7	1.00
H(6a)'	753	575	293	5.0	0.94
H(6b)'	647	456	322	5.0	1.08
H(7a)	732	444	419	5.2	0.99
H(7b)	882	456	439	5.2	1.06
H(10a)	975	263	187	4.0	0.83
H(10b)	926	160	108	4.0	0.99
H(11a)	820	424	119	4.3	0.99
H(11b)	744	253	100	4.3	1.00
H(11a)'	918	438	244	4.0	0.95
H(11b)'	843	452	141	4.0	1.00
H(14)	623	-110	405	2.3	0.94
H(16)	709	-339	659	2.9	1.00
H(17)	921	-309	629	3.9	0.96
H(18)	966	-172	502	3.4	0.97

taken from ref. 4. All calculations were performed on a PDP 11/34 (64 K) computer using the Enraf-Nonius SDP program-package and local programs. Final atomic parameters are given in Tables 1 and 2.

Discussion

A molecular diagram with the numbering of the atoms is depicted in Fig. 1. The molecular structure as viewed down the N(5)→Si(1) axis is shown in Fig. 2. Bond lengths and angles are listed in Table 3.

The molecule possesses the usual silatrane skeleton containing a five-coordinated silicon atom. The transannular N→Si dative bond length is rather short (2.079(2) Å), and this can be attributed to the electron-withdrawing substituent present on silicon in the apical position. The N→Si bond in the title compound is the second shortest reported so far (an N→Si bond of 2.023 Å was found in chlorosilatrane [5]).

The silicon atom is surrounded by four oxygen atoms. The mean Si—O(eq) bond distance is 1.656(4) Å, and individual Si—O bond lengths vary over an interval of 0.015 Å. The asymmetric chlorophenoxy group seems to disturb the three-fold symmetry of the silatrane skeleton. The H(14) *ortho*-hydrogen atoms forms a close Van der Waals contact of 2.44 Å with O(2) which maintains the longest Si—O bond (1.664(2)) of the equatorial oxygen atoms. (The torsion angles describing the position of the chlorophenoxy group relative to the equatorial oxygen atoms are as follows: O(2)—Si(1)—O(12)—C(13): -68.9(4); O(8)—Si(1)—O(12)—C(13): 50.6(3); O(9)—Si(1)—O(12)—C(13): 171.3(4)°.) The apical Si—O(12) bond is considerably longer (1.690(2) Å), though it is

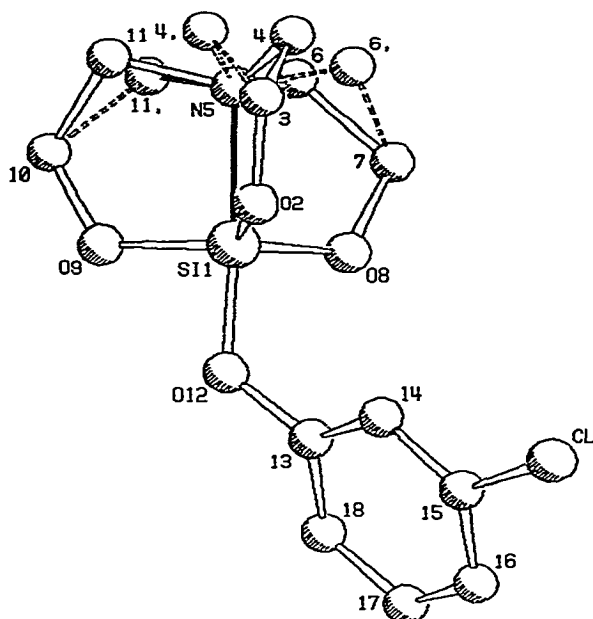


Fig. 1. The diagram of the molecule with the numbering of atoms, hydrogen atoms are omitted for clarity. Bare numbers represent carbon atoms. (Carbon atoms marked with a comma have a multiplicity of 0.20).

somewhat shorter than the Si—O(C=O) bonds found in silatranones (1.720(2) Å, [1]). The bond angle at O(12) is also larger (129.7(3)°) than the mean Si—O(eq)—C angle (121.5(2)°). The *m*-chlorophenoxy group is tilted with respect to the silatrane moiety: it forms a dihedral angle of -57.4° with the plane of O(2), O(8), O(9) atoms (cf. Table 4).

The partial disorder is well resolved and the positions of the disordered carbon atoms are quite regular with respect to other atoms in the silatrane moiety. The arrangements of the Si(1), O(8), C(7), N(5) and Si(1), O(9), C(10),

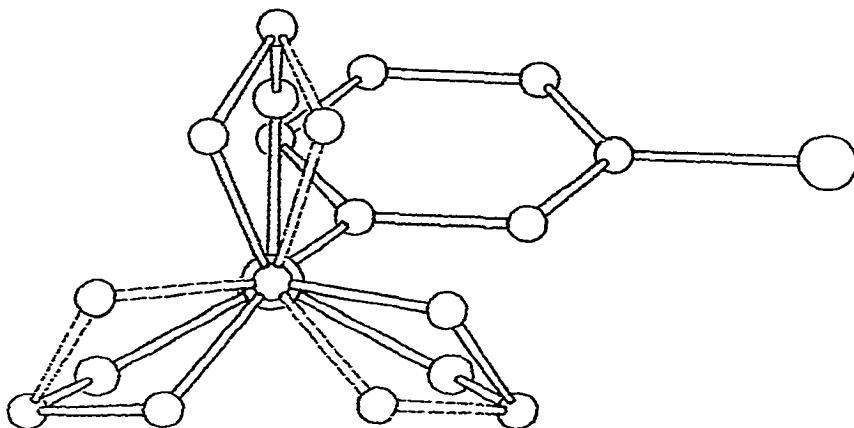


Fig. 2. The molecular structure as viewed down the N→Si bond axis. Hydrogen atoms are omitted for clarity.

TABLE 3
BOND DISTANCES (Å) AND ANGLES (°) WITH THEIR E.S.D.'s

Si(1)—O(2)	1.664(2)	C(6)—C(7)	1.568(4)
Si(1)—N(5)	2.079(2)	C(6)'—C(7)	1.46(1)
Si(1)—O(8)	1.656(2)	C(7)—O(8)	1.418(4)
Si(1)—O(9)	1.649(2)	O(9)—C(10)	1.427(3)
Si(1)—O(12)	1.690(2)	C(10)—C(11)	1.533(5)
O(2)—C(3)	1.420(3)	C(10)—C(11)'	1.57(1)
C(3)—C(4)	1.501(5)	O(12)—C(13)	1.352(3)
C(3)—C(4)'	1.59(1)	C(13)—C(14)	1.392(4)
C(4)—N(5)	1.488(4)	C(13)—C(18)	1.400(4)
C(4)'—N(5)	1.46(1)	C(14)—C(15)	1.382(4)
N(5)—C(6)	1.467(4)	C(15)—C(16)	1.376(4)
N(5)—C(6)'	1.52(1)	C(15)—Cl	1.750(3)
N(5)—C(11)	1.492(4)	C(16)—C(17)	1.391(5)
N(5)—C(11)'	1.49(1)	C(17)—C(18)	1.388(4)
O(2)—Si(1)—O(8)	118.3(2)	C(4)'—N(5)—C(11)'	114(1)
O(2)—Si(1)—O(9)	119.4(2)	C(6)—N(5)—C(11)	113.1(4)
O(2)—Si(1)—O(12)	96.8(2)	C(6)'—N(5)—C(11)'	106(1)
O(8)—Si(1)—O(9)	120.3(2)	N(5)—C(6)—C(7)	104.1(5)
O(8)—Si(1)—O(12)	96.0(2)	N(5)—C(6)'—C(7)	107(2)
O(9)—Si(1)—O(12)	91.4(2)	C(6)—C(7)—O(8)	109.2(4)
O(2)—Si(1)—N(5)	85.3(2)	C(6)'—C(7)—O(8)	113(1)
O(8)—Si(1)—N(5)	85.5(2)	Si(1)—O(8)—C(7)	121.6(3)
O(9)—Si(1)—N(5)	85.2(2)	Si(1)—O(9)—C(10)	121.8(3)
O(12)—Si(1)—N(5)	176.5(2)	O(9)—C(10)—C(11)	109.9(4)
Si(1)—O(2)—C(3)	121.2(3)	O(9)—C(10)—C(11)'	109(1)
O(2)—C(3)—C(4)	110.3(4)	C(10)—C(11)—N(5)	104.1(4)
O(2)—C(3)—C(4)'	110(1)	C(10)—C(11)'—N(5)	103(1)
C(3)—C(4)—N(5)	106.1(5)	Si(1)—O(12)—C(13)	129.7(3)
C(3)—C(4)'—N(5)	103(1)	O(12)—C(13)—C(14)	122.1(4)
C(4)—N(5)—Si(1)	105.2(3)	O(12)—C(13)—C(18)	118.5(4)
C(4)'—N(5)—Si(1)	108(1)	C(14)—C(13)—C(18)	119.4(4)
C(6)—N(5)—Si(1)	105.9(3)	C(14)—C(15)—C(16)	123.2(5)
C(6)'—N(5)—Si(1)	106(1)	C(14)—C(15)—Cl	118.2(4)
C(11)—N(5)—Si(1)	105.7(3)	C(16)—C(15)—Cl	118.6(4)
C(11)'—N(5)—Si(1)	105(1)	C(15)—C(16)—C(17)	117.5(5)
C(4)—N(5)—C(6)	115.1(4)	C(16)—C(17)—C(18)	121.1(5)
C(4)'—N(5)—C(6)'	117(1)	C(13)—C(18)—C(17)	120.0(4)
C(4)—N(5)—C(11)	111.0(4)		
Relevant mean bond angles (°)			
Si—O(eq)—C	121.5(2)	C—N→Si	105.6(2)
O(eq)—Si—O(eq)	119.3(6)	C'—N→Si	106(1)
O(eq)—Si—O(ap)	94.7(1.7)	C—N—C	113.1(1.2)
O(eq)—Si←N	85.3(1)	C'—N—C'	112(3)

N(5) atoms are exactly planar, while the Si(1), O(2), C(3), N(5) moiety is fairly planar (definitions of planes, plane equations and dihedral angles are shown in Table 4.) Disordered atoms are situated on both sides of these planes as mirror-images. Similar disorder was reported for α -1-phenyl silatrane [6] and two other silatrane analogues [7,8]. In all cases carbon atoms attached to nitrogen are involved in the partial disorder. These atoms generally deviate from the planes formed by other atoms of the chains connecting silicon and nitrogen. Such disorder may be due to the internal motion (ring inversion) of the SiOCCN rings.

It has been shown earlier for silatranes [9,5,10] that with increasing N→Si

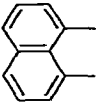
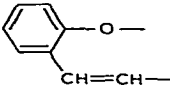
TABLE 4

LEAST SQUARES PLANES. (The equation of plane is given in the form: $ax + by + cz - d = 0$, where x, y, z are orthogonalized coordinates)

Plane	Atoms forming the plane	a	b	c	d	Mean deviation from plane (Å)	Distance of other atoms from plane (Å)			
1	O(2), O(8), O(9)	-0.1541	0.8542	-0.4965	-2.5911	—	Si(1) -0.186(1)			
2	C(4), C(6), C(11)	-0.1599	0.8523	-0.4979	-0.3078	—	N(5) -0.398(2)			
3	C(4), C(6), C(11)	-0.1373	0.8591	-0.4930	-0.0694	—	N(5) -0.416(2)			
4	Si(1), O(2), C(3), N(5)	0.4102	-0.4082	-0.8155	-0.4997	0.006	C(4) -0.492(4)			
							C(4)' 0.51(1)			
5	Si(1), O(8), C(7), N(5)	0.9844	0.0888	-0.1517	7.7835	0.000	C(6) 0.543(4)			
							C(6)' -0.40(2)			
6	Si(1), O(9), C(10), N(5)	-0.5797	-0.4867	-0.6535	-8.2687	0.000	C(11) 0.535(4)			
							C(11)' -0.60(1)			
7	C(13), C(14), C(15), C(16), C(17), C(18)	0.0394	-0.8885	-0.4571	-1.6320	0.003	O(12) 0.074(2)			
							Cl -0.039(1)			
Dihedral angles (°)										
1-2	0.4	1.0	1-4	-89.6	1-5	-90.0	1-6	-89.9	1-7	-57.4
		1.4	2-4	-89.6	2-5	-89.6	2-6	89.8	2-7	-57.6
			3-4	-89.7	3-5	89.1	3-6	-89.1	3-7	-57.1
					4-5	60.6	4-6	60.4	4-7	41.3
							5-6	-59.0	5-7	88.3
									6-7	44.9

TABLE 5

SOME GEOMETRICAL DATA CHARACTERISING THE STEREOCHEMISTRY OF SILICON AND NITROGEN IN SILATRANES, SILATRANE ANALOGUES AND DIOXA-AZA-SILACYCLOOCTANES

$\overline{\text{R}}\text{Si}(\text{OCH}_2\text{CH}_2)_n(\text{XCR}'\text{CH}_2)_{3-n}\text{N}$							
R	n	X	R'	$d(\text{Si}\leftarrow\text{N})$ (Å)	ΔSi (Å)	ΔN (Å)	Ref
Cl	3			2.023	0.10	0.40	5
<i>m</i> -ClC ₆ H ₄ O	3			2.079(2)	0.14	0.40	this work
<i>m</i> -CF ₃ C ₆ H ₄	2	O	O	2.106(3)	0.19	0.39	1
<i>m</i> -NO ₂ C ₆ H ₄	3			2.116(8)	0.17	0.39	11
ClCH ₂	3			2.120	0.16	0.35	12
ClCH ₂	1	O	HCH ₃	2.12(1)	0.17	0.38	13
C ₆ H ₅ COOCH ₂	3			2.122(7)	0.16	0.36	14
<i>p</i> -FC ₆ H ₄	2	O	O	2.129(3)	0.20	0.39	1
γ -C ₆ H ₅	3			2.132(4)	0.18	0.39	9
β -C ₆ H ₅	3			2.156(4)	0.20	0.38	15
CH ₃	3			2.175(4)	0.21	0.38	16
ClCH ₂ CH ₂ CH ₂	3			2.18	0.20		17
α -C ₆ H ₅	3			2.193(5)	0.20	0.34	6
C ₂ H ₅	3			2.21	0.23		18
CH ₃ O	2	CH ₂	H ₂	2.223(5)	0.23	0.37	19
CH ₃	2	CH ₂	H ₂	2.336(4)	0.29	0.35	20
C ₆ H ₅	— ^a			2.344(5)	0.29	0.29	21
[(C ₆ H ₅)(CH ₃) ₂ P] ₂ Pt(Cl)	3			2.89(1)	0.53	0.07	22
$\text{R}_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}'$							
R ₂	R'	$d(\text{Si}\leftarrow\text{N})$ (Å)	ΔSi (Å)	ΔN (Å)	Ref		
	CH ₃	2.263(6)	0.16		23		
	CH ₃	2.297(6)			7		
(C ₆ H ₅) ₂	H	2.301(6)	0.25	0.31	24		
(C ₆ H ₅) ₂	CH ₃	2.68(1)	0.38	0.38	25		
(C ₆ H ₅) ₂	C ₆ H ₅	3.08(1)	0.48	0.16	25		
(C ₆ H ₅) ₂	C(CH ₃) ₃	3.16(2)	0.49	0.42	25		
(CH ₃) ₂	C ₆ H ₅	3.19(1)	0.51	0.12	25		

^a (OC₆H₄)₃.

distance the trigonal bipyramidal stereochemistry of silicon becomes more tetrahedral while the tetrahedron around nitrogen flattens out. A compilation of structural data gave rise to the diagram depicted in Fig. 3. The numerical data are given in Table 5. An increase in the N→Si distance is accompanied by increasing deviation of silicon from the plane of the equatorial atoms (usually oxygens) in a direction away from the nitrogen atom. Nitrogen, on the other hand, moves towards the plane of its substituent atoms. The equation of the least-squares line for the ΔSi data is $\Delta\text{Si} = 0.478d(\text{Si}-\text{N}) - 0.840$, the regres-

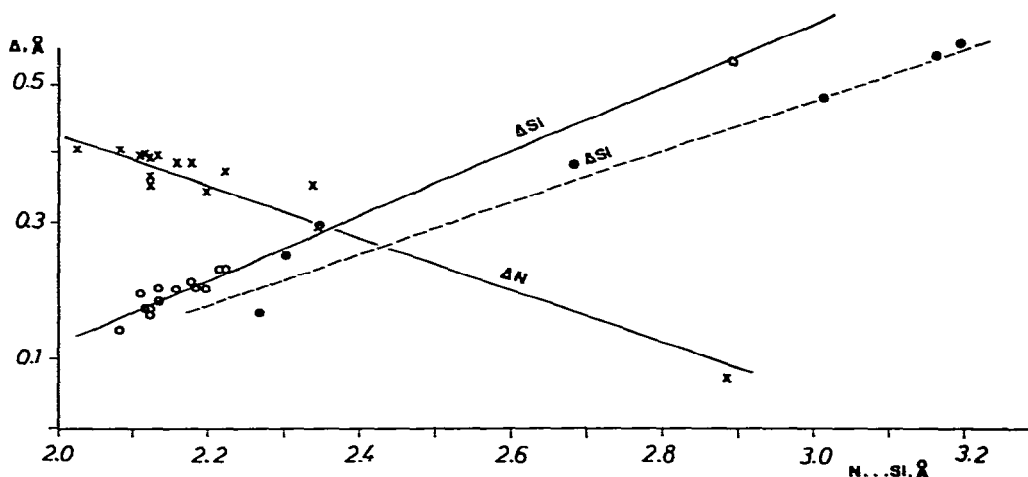


Fig. 3. The distance of silicon from the plane of the equatorial atoms (ΔSi) and the distance of nitrogen from the plane of the neighbouring carbon atoms (ΔN) plotted against the $N \cdots Si$ approach. The dashed line refers to dioxazasilacyclooctane data.

sion coefficient $R = 0.989$, for ΔN data: $\Delta N = -0.385d(Si-N) + 1.200$, $R = 0.966$. The distortion of the tetrahedron around nitrogen is probably induced by the geometric strains of the (usually) ethoxy-chains. When the three-fold coupling is not achieved (cf. the relevant data for the related bicyclic compounds, dioxazasilacyclooctanes, in Table 5) no such correlation may be established for ΔN . Three of the six dioxazasilacyclooctane molecules have $N \cdots Si$ approaches longer than 3.0 \AA , and such a separation excludes the existence of any kind of bonding between silicon and nitrogen. The molecular structures indicate, however, that the lone pair of the nitrogen atom still points towards the silicon atom. Thus a correlation, similar to the tricyclic compounds, seems to hold for the stereochemistry of silicon ($\Delta Si = 0.331d(Si-N) - 0.542$, $R = 0.978$) showing that such a correlation is not accidental.

The changes in the stereochemistry of silicon in silatranes as a function of the $N \cdots Si$ approach may be suggestive of the geometrical changes undergone by a molecule in a chemical reaction (c.f. [26,27]). Silatranes and related compounds may serve as examples of the geometric changes that take place in an S_N2 -type ligand-exchange reaction $\equiv Si-X + HN \equiv \rightarrow \equiv Si-N \equiv$ with the various crystal structures representing different stages along the reaction coordinate.

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