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CRYSTAL AND MOLECULAR STRUCTURE OF γ-1-PHENYLSILATRANE: SOME STRUCTURAL FEATURES OF SILATRANES

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Summary

γ-1-phenylsilatrane crystallizes in the monoclinic space group $P2_1/n$, with a 8.475, b 12.949, c 11.122 Å and β 90.86°. The structure was determined by direct methods and was refined to R 0.078 for 1687 observed reflexions and 0.081 for all 1813 reflexions. The N→Si bond length is 2.132(4), Si—C is 1.894(5) Å. The mean Si—O bond distance is 1.656 Å, angle N—Si—C is 179.0(2)°. The average N—Si—O, C—Si—O and O—Si—O angles are 83.6, 96.4 and 123.5°. By use of published data for six other silatrane molecules, some structural features were established. Thus, the length of the N→Si bond is affected by the other apical substituents of the silicon atom, the number of oxygen atoms attached to it and steric effects. Increase in the length of the dative N→Si bond is accompanied by further distortion of the trigonal bipyramidal configuration and of the tetrahedron around the nitrogen atom. The relatively long Si—C(sp^2) bond may be due to decreased d_π—p_π interaction. The crystalline modifications (α, β, γ) of the 1-phenyl-derivative possibly result from rapid ring-inversion in solution.

Introduction

In an earlier paper [1] we reported the existence of two crystallographically distinct forms of 1-phenyl-silatrane [(2,2',2''-nitrilotriethoxy)phenylsilane] and we discussed the structure of the β-form, which was of the same conformation as found for the disordered α-modification [2] but contained a significant-

TABLE 1

THE FINAL ATOMIC PARAMETERS ($\times 10^4$) WITH THEIR ESD's IN PARENTHESES

Anisotropic thermal parameters are given in the form:
$T = \exp[-(b_{11}'h^2 + b_{22}'k^2 + b_{33}'l^2 + b_{12}'h'k + b_{13}'h'l + b_{23}'k'l)]$

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Si	1067(2)	3217(1)	2191(1)	75(2)	48(1)	49(1)	4(2)	6(2)	4(1)
O(2)	896(4)	2742(3)	3564(3)	140(5)	73(3)	56(3)	75(6)	37(7)	27(5)
C(3)	1763(7)	1877(5)	4004(5)	161(9)	81(4)	77(5)	104(10)	50(11)	56(7)
C(4)	3297(7)	1790(5)	3296(5)	146(8)	84(4)	59(4)	77(10)	10(10)	17(7)
N	2898(5)	2095(3)	2061(4)	99(6)	52(3)	60(3)	21(7)	13(8)	9(5)
C(6)	2178(7)	1241(5)	1361(5)	165(9)	51(3)	75(5)	26(9)	−25(11)	−13(7)
C(7)	1060(7)	1754(5)	442(5)	142(8)	62(4)	81(5)	33(9)	−11(11)	−24(7)
O(8)	276(4)	2574(3)	1040(3)	116(5)	56(2)	73(3)	18(6)	−22(7)	−23(5)
O(9)	2497(4)	4046(3)	1904(4)	82(5)	57(2)	106(4)	−14(6)	29(7)	−1(5)
C(10)	4123(6)	3756(3)	1851(7)	90(7)	64(4)	140(7)	8(9)	47(11)	−17(9)
C(11)	4194(7)	2606(5)	1421(6)	113(7)	65(4)	97(5)	11(9)	64(11)	−3(8)
C(12)	−535(6)	4229(4)	2321(5)	84(6)	52(3)	61(4)	−11(8)	5(8)	7(6)
C(13)	−984(7)	4635(5)	3426(5)	119(7)	63(4)	75(4)	18(9)	43(10)	−1(7)
C(14)	−2056(7)	5441(5)	3499(6)	125(8)	73(4)	108(6)	28(10)	56(12)	−18(8)
C(15)	−2704(7)	5877(5)	2476(7)	96(7)	63(4)	131(6)	7(9)	3(12)	1(9)
C(16)	−2294(7)	5476(5)	1362(6)	109(8)	65(4)	116(6)	18(9)	−39(12)	26(8)
C(17)	−1240(6)	4671(5)	1289(5)	92(7)	57(3)	81(5)	−5(8)	−22(10)	16(7)

ly shorter N→Si bond [2.156(4) Å]. In order to establish the structural differences in all three forms an X-ray structure analysis of the γ-modification was performed.

Experimental

Crystal data

$C_{12}H_{17}O_3NSi$, mol. wt. 251.36, m.p. 207°C. The crystals are colourless needles elongated along the *b* axis. *a* 8.475(1), *b* 12.949(2), *c* 11.122(4) Å; β 90.86(2)°. *V* 1220.69 Å^3, *Z* 4. D_m 1.364 g cm^{-3} (by flotation), D_x 1.368 g cm^{-3}. *F*(000) 536; monoclinic space group $P2_1/n$ (no. 14), μ for Cu-K_α (λ 1.5418 Å) 16.75 cm^{-1}.

Unit cell dimensions were determined from zero-layer precession photographs.

The crystal used for the intensity data collection was approximately 0.45 × 0.20 × 0.10 mm. Intensities were collected on a Stoe two-circle semi-automatic diffractometer in the equi-inclination arrangement for the $h0l \rightarrow h,12,l$ layers by the ω-scanning method, with Cu-K_α radiation and scintillation counter (Ni-filter and pulse-height discriminator). 126 of the 1813 reflexions with $I - 1.5\ \sigma\ (I) \leqslant 0$ were taken as unobserved with a value of $I_0 = 0.5\ \sigma\ (I)$. After data reduction an absolute scale factor and overall temperature factor (*B* 2.69 Å^2) were determined by Wilson's method. No absorption correction was applied.

Structure determination and refinement

The structure was solved by direct methods with the MULTAN program [3]. 279 reflexions with *E*-values greater than 1.4 were used. An *E*-map based on the phases of these reflexions revealed the positions of all the 17 non-hydrogen atoms which gave an *R*-value 0.31 [$R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$]. These coordinates

TABLE 2

FRACTIONAL COORDINATES (×10^3), ISOTROPIC TEMPERATURE PARAMETERS (Å^2) AND BOND DISTANCES (Å) FOR THE HYDROGEN ATOMS

	x/a	*y/b*	*z/c*	*B*	C—H distances
H(3a)	201	197	487	4.3	0.99
H(3b)	112	124	389	4.3	1.00
H(4a)	409	229	364	3.5	1.00
H(4b)	367	106	331	3.5	1.00
H(6a)	155	78	181	3.4	0.94
H(6b)	302	86	93	3.4	1.00
H(7a)	27	124	15	3.6	1.00
H(7b)	169	204	—24	3.6	1.00
H(10a)	462	383	266	3.8	0.99
H(10b)	466	421	124	3.8	1.00
H(11a)	523	230	168	3.9	1.00
H(11b)	400	257	53	3.9	1.00
H(13)	—25	481	412	3.3	1.01
H(14)	—272	523	420	4.2	1.00
H(15)	—345	648	253	3.9	1.00
H(16)	—304	531	68	4.3	1.01
H(17)	—60	489	58	3.0	1.00

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) WITH THEIR ESD's IN PARENTHESES

Si—O(2)	1.655(4)	At Si					
Si—O(8)	1.660(4)	O(2)—Si—O(8)	119.03(20)	C(12)—Si—O(2)	96.55(21)	N—Si—C(12)	179.01(20)
Si—O(9)	1.654(4)	O(2)—Si—O(9)	119.60(20)	C(12)—Si—O(8)	97.14(21)	N—Si—O(2)	83.29(18)
Si—N	2.132(4)	O(8)—Si—O(9)	117.74(20)	C(12)—Si—O(9)	95.39(21)	N—Si—O(8)	83.79(18)
Si—C(12)	1.894(5)					N—Si—O(9)	83.86(18)
O(2)—C(3)	1.422(7)						
O(8)—C(7)	1.423(7)						
O(9)—C(10)	1.430(7)						
C(3)—C(4)	1.534(9)						
C(6)—C(7)	1.535(9)						
C(10)—C(11)	1.565(9)						
N—C(4)	1.464(7)						
N—C(6)	1.479(7)						
N—C(11)	1.475(7)						
C(12)—C(13)	1.395(8)						
C(13)—C(14)	1.387(9)						
C(14)—C(15)	1.377(9)						
C(15)—C(16)	1.392(9)						
C(16)—C(17)	1.376(9)						
C(17)—C(12)	1.408(8)						

At N		In ethoxy bridges		In the phenyl group	
C(4)—N—C(6)	112.33(43)	Si—O(2)—C(3)	123.94(36)	Si—C(12)—C(13)	122.23(40)
C(4)—N—C(11)	114.25(43)	Si—O(8)—C(7)	123.28(35)	C(13)—C(14)—C(15)	120.91(60)
C(6)—N—C(11)	112.70(43)	Si—O(9)—C(10)	123.15(36)	C(15)—C(16)—C(17)	120.39(58)
C(4)—N—Si	106.16(33)	O(2)—C(3)—C(4)	108.58(48)	C(17)—C(12)—C(13)	116.56(48)
C(6)—N—Si	104.49(32)	O(8)—C(7)—C(6)	107.44(47)	C(12)—C(13)—C(14)	121.52(54)
C(11)—N—Si	105.97(33)	O(9)—C(10)—C(11)	107.68(48)	C(14)—C(15)—C(16)	118.73(61)
		C(3)—C(4)—N	106.03(47)	C(16)—C(17)—C(12)	121.87(52)
		C(7)—C(6)—N	105.83(46)	C(17)—C(12)—Si	121.00(39)
		C(10)—C(11)—N	104.31(46)		

were then refined using the program of Albano et al. [4]. The function minimized was $\Phi = w_h(|F_o| - 1/G|F_c|)^2$, where w_h is the weighting scheme of Cruickshank et al. [5], and G is the scaling factor $[w_h = (8.0 + 1.0\ F_0 + 0.01\ F_0^2)^{-1}]$ After three isotropic and two anisotropic cycles of block-diagonal matrix refinement (R 0.109) the positions of the hydrogen atoms were geometrically generated assuming the appropriate sp^2 or sp^3 hybridization of the carbon atoms. Two further anisotropic cycles of refinement reduced R to the final value of 0.078 for observed and 0.081 for all reflexions. At this state the maximum shifts in the atomic coordinated were less than 0.5 σ_{av}. No hydrogen parameters were refined. The isotropic thermal parameters of the hydrogen atoms were approximated by those of the carbon atoms. The final atomic parameters for the non-hydrogen atoms are given in Table 1 and hydrogen atomic coordinates, isotropic thermal parameters and C—H distances in Table 2. Scattering factors were taken from International Tables for X-ray Crystallography [6] *.

Results and discussion

The bond lengths and angles are given in Table 3. Fig. 1 is a diagram of the molecule.

The distorted trigonal bipyramidal geometry of the molecule is fairly similar to those of the α- and β-forms and related compounds. The length of the transannular N→Si dative bond in the γ-form is the shortest of the three modifications [2.132(4) Å].

The results of structure analyses of silatranes, including the present work, provide data for a comparison in order to throw light upon some geometric fea-

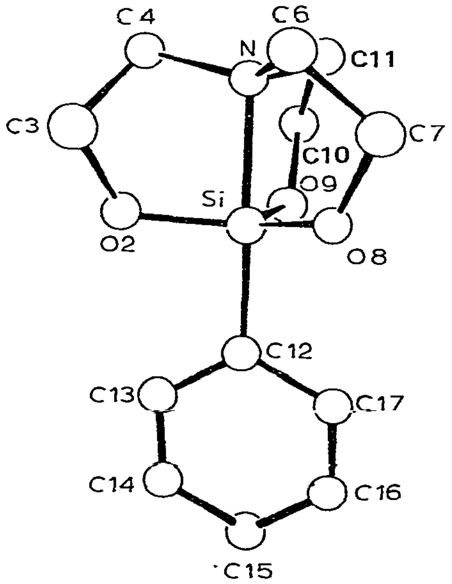

Fig. 1. Molecular geometry and atomic numbering.

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* The table of structure factors can be obtained from the authors on request.

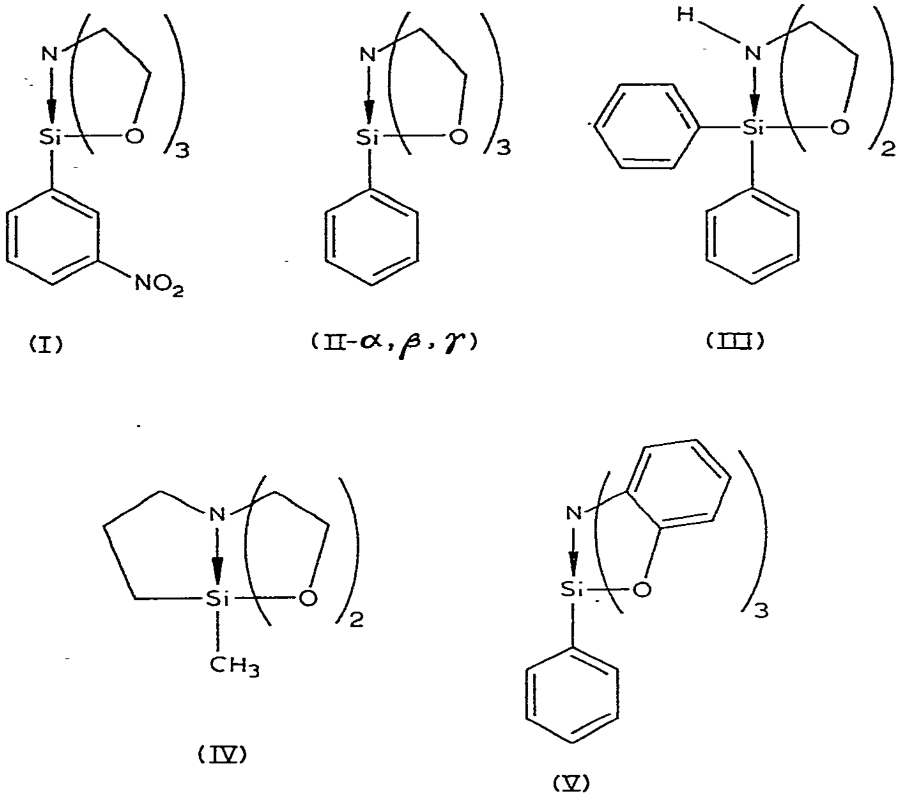

Fig. 2. Chemical formulae.

tures characteristic of these five-coordinated silicon compounds. The structures used in the discussion are shown in Fig. 2. The relevant structural parameters are summarized in Table 4 in order of increasing N→Si bond length. We note that compounds III and V are significantly different systems.

Boer and Turley pointed out earlier [9] that the N→Si bond length shows great variety in silatranes and the relatively long $C(sp^2)$—Si bond length is also a peculiarity of structures I, II-α, IV and V.

The formation of the characteristic silatrane structure may be clearly depicted by considering a positively charged silicon atom acting as a Lewis acid under the influence of three oxygen atoms. This positive silicon readily interacts with the relevant Lewis base, i.e. the lone pair of the nitrogen atom. The resulting dative N→Si bond leads to a relatively large electron density upon the silicon atom. The length (and strength) of this "hypervalent" [11] bond is very sensitive to electronic interactions, and to steric effects.

The electron withdrawing *m*-nitro group attached to the phenyl substituent further increases the positive charge on the silicon and so a strong dative bond is formed in I.

These molecules show rapid ring-inversion in solution (as studied extensively in solutions of stannatranes [12]) and we assume that crystalline modifications of II are composed of molecules frozen in the solid state as different stages of

TABLE 4

GEOMETRIC DATA FOR DIFFERENT SILATRANE STRUCTURES

Compound	Bond lengths (Å)		Mean bond lengths (Å)		Bond angles (°)		Mean bond angles (°)				Si—Plane[b] (Å)	Ref.
	N→Si	Si—C(sp^2)	Si—O	C(sp^3)—C(sp^3)	N—Si—C	C—Si—O	N—Si—O	Si—O—C	C—N—C	C—N—Si		
I	2.116(6)	1.905(9)	1.656	1.511	179.0	95.8	84.1	122.6	113.2	105.4	0.170	7
II-γ	2.132(4)	1.894(5)	1.656	1.545	179.0	96.4	83.6	123.5	113.1	105.5	0.183	this work
II-β	2.156(4)	1.908(4)	1.657	1.487	177.0	96.8	83.2	122.8	113.6	105.0	0.195	1
II-α	2.193(5)	1.882(6)	1.656	1.498	177.9	97.1	82.3	123.4	113.8	104.5	0.204	2
III	2.301(6)	1.901(6) (ax.) 1.886(7) (eq.)	1.652	1.390	174.0	97.0 (ax.)	80.3	124.8	112.8	103.3	0.248	8
IV	2.336(4)	1.857(5)[a]	1.666	1.508	176.8	98.0	80.2	123.1	114.4	103.9	0.294	9
V	2.344(4)	1.853(6)	1.640	—	179.4	100.1	79.9	125.9	116.0	102.0	0.290	10

[a] Corrected for the proper (sp^2) base [9]. [b] The normal distance of silicon from the plane of the three equatorial atoms.

ring-inversion. The N→Si bond, being the weakest bond, may stretch when ring-inversion occurs. Comparison of the various structures, leads to the following conclusions.

(a) The variation in the N→Si bond lengths is significant (Table 4).

(b) C(sp^3)—C(sp^3) bond lengths are short, with the exception of II-γ. Short aliphatic C—C bond distances are quite usual in these structures and in structures of similar molecular geometry (e.g. 1-α-naphthylgermatrane [13] or the 2,2′,2″-trimethoxytriethylamine—NaI complex [14]).

In compounds III and IV there are only two oxygens bound to the silicon atom, and so a weaker N→Si bond results.

The five-membered rings in V are planar, and the phenoxy groups inductively reduce the basicity of the nitrogen atom [10]. The result is a weak N→Si bond.

The *d*-orbital participation in the formation of the silatrane structures reduces the extent of the considerable d_π—p_π interaction between the phenyl ring and the silicon and between the oxygen atoms and silicon. In molecules having N→Si bond lengths shorter than ca. 2.16 Å, is found the maximum length of the Si—C(sp^2) bond (about 1.90 Å), and with increasing length of the dative bond, the Si—C(sp^2) bond distances tend to shorten with the exception of III which contains two phenyl groups. It is instructive to compare these bond distances with those in $PhSiH_3$ (1.843(5) Å [15], maximum d_π—p_π character) and Ph_4Si (mean value 1.869 Å [16,17]). The Si—O bond distances are relatively long for the same reason, and these bonds do not alter substantially in the examples cited. The mean value is 1.623 in $[SiO_4]_x$ tetrahedral [18], 1.634(2) in disiloxane [19], 1.640(3) in methoxysilane [20], and 1.648(7) Å in phenoxysilane [20].

Lengthening of the N→Si bond is accompanied by further distortion of the trigonal bipyramid around silicon, as revealed by the C—Si—O, N—Si—O mean bond angles and by the increasing deviation of the silicon atom from the plane of the equatorial atoms.

A flattened tetrahedron is formed around the nitrogen atom (cf. the C—N—C and C—N—Si mean bond angles) as a consequence of the donation of the lone pair to the silicon. This flattening is more extensive the greater the N→Si distance. The increase in the N→Si distance occurs partly at the expense of the distortion of the tetrahedron around the nitrogen and the plane containing the silicon and the three equatorial substituents. The former is distorted to a more planar and the latter towards a tetrahedral configuration.

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