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THE CRYSTAL STRUCTURE OF A CYCLO-SILAZOXANE, $[(Me_2Si)_2ONC_6F_5]_2$

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Summary

Crystals of the silazoxane, $[(Me_2Si)_2ONC_6F_5]_2$ are triclinic with a 8.703(4), b 14.334(6), c 13.021(6) Å, α 102.05(3), β 107.43(4) and γ 105.83(4)°, space group $P\bar{1}$, $Z = 2$. The asymmetric unit consists of two half molecules, each of which lies on a centre of symmetry. Each of the rings has a chair conformation with mean Si—N and Si—O distances of 1.747 and 1.623 Å respectively; the endocyclic angles at the silicon atoms in the asymmetric unit are different (mean values 109.6 and 106.3°) and the ring angles at oxygen and nitrogen have mean values of 147.7 and 123.2° respectively.

Introduction

Although the cyclo-silazanes, $(R_2SiN)_{2,3\text{ and }4}$ [1—8] and cyclo-siloxanes, $(R_2SiO)_{3\text{ and }4}$ [9] have been extensively investigated, there is little information on the related, mixed silicon-nitrogen-oxygen heterocycles. The chemistry of

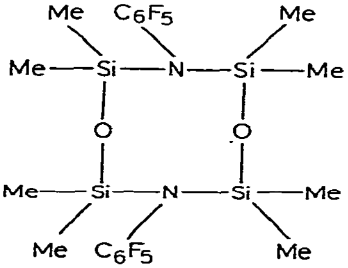

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TABLE 1

FRACTIONAL ATOMIC COORDINATE (X 10^4) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{iso}
Si(1)	4080(1)	940.3(7)	5817.7(7)	
Si(2)	3605(1)	223.8(7)	3275.2(7)	
O(1)	3365(3)	306(2)	4473(2)	
N(1)	5382(3)	—154(2)	3386(2)	
C(1)	6428(4)	200(2)	2799(3)	
C(2)	6006(4)	—280(3)	1666(3)	
C(3)	7040(6)	55(3)	1088(3)	
C(4)	8501(6)	889(4)	1639(4)	
C(5)	8972(5)	1389(3)	2749(4)	
C(6)	7939(5)	1041(3)	3320(3)	
C(7)	2321(5)	1293(3)	6100(3)	
C(8)	6020(5)	2072(3)	6186(3)	
C(9)	1581(5)	—733(3)	2163(3)	
C(10)	4069(5)	1465(3)	3002(3)	
F(2)	4553(3)	—1098(2)	1095(2)	
F(3)	6562(4)	—454(2)	—14(2)	
F(4)	9493(4)	1211(2)	1075(3)	
F(5)	10413(3)	2206(2)	3300(3)	
F(6)	8446(3)	1532(2)	4422(2)	
Si(3)	6169(1)	6083.1(6)	9432.8(7)	
Si(4)	7644(1)	4854.0(8)	10929.6(8)	
O(2)	6850(2)	5234(2)	9872(2)	
N(2)	6012(3)	4477(2)	11442(2)	
C(11)	6482(4)	4660(2)	12625(2)	
C(12)	6171(4)	5414(3)	13299(3)	
C(13)	6617(5)	5599(3)	14448(3)	
C(14)	7405(5)	5029(3)	14960(3)	
C(15)	7735(5)	4276(3)	14337(3)	
C(16)	7273(4)	4096(3)	13185(3)	
C(17)	6451(5)	7103(3)	10675(3)	
C(18)	7399(4)	6591(3)	8618(3)	
C(19)	9507(5)	5891(4)	12075(4)	
C(20)	8266(6)	3784(4)	10367(4)	
F(12)	5390(3)	5989(2)	12818(2)	
F(13)	6253(3)	6329(2)	15052(2)	
F(14)	7846(4)	5203(2)	16081(2)	
F(15)	8510(3)	3705(2)	14833(2)	
F(16)	7597(3)	3342(2)	12594(2)	
H(71)	1277	655	5884	50
H(72)	2693	1671	6921	50
H(73)	1967	1733	5636	50
H(81)	6969	1866	6032	50
H(82)	6482	2479	7021	50
H(83)	5755	2540	5735	50
H(91)	1332	—1413	2321	50
H(92)	574	—508	2147	50
H(93)	1652	—847	1397	50
H(101)	5183	1986	3616	50
H(102)	3117	1736	3002	50
H(103)	4195	1397	2252	50
H(171)	5769	6824	11117	50
H(172)	7703	7443	11201	50
H(173)	6043	7649	10432	50
H(181	7239	6020	7943	50
H(182)	8672	6911	9104	50
H(183)	7012	7117	8336	50
H(191)	9135	6477	12377	50
H(192)	9995	5653	12727	50
H(193)	10431	6176	11798	50
H(201)	7205	3209	9723	50
H(202)	8714	3477	10960	50
H(203)	9150	4000	10031	50

these compounds, which are known as trimers and tetramers, was reviewed in 1969 by Haiduc [10] but the structures of only three such compounds have been determined [11—13]. A number of silazoxanes containing the C_6F_5 group are known [14] and to provide more information on these mixed species, the structure of 1,1,3,3,5,5,7,7-octamethyl-2,6-bis(pentafluorophenyl)-cyclo-1,3,5,7-tetrasila-2,6-diaza-4,8-dioxane (**1**) has been determined.

Structure determination

Crystal data. $C_{20}H_{24}F_{10}N_2O_2Si_4$, M = 626, triclinic a 8.703(4), b 14.334(6), c 13.021(6) Å, α 102.05(3), β 107.43(4), γ 105.83(4)°, U 1605.1 Å^3, $Z = 2$, D_c 1.30 g ml^{-1}, D_m ca. 1.4 g ml^{-1}, $F(000) = 640$, Mo-K_α radiation λ 0.7107 Å, μ(Mo-K_α) 2.7 cm^{-1}.

TABLE 2

ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$) with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	53.3(5)	50.3(5)	50.0(5)	17.0(4)	18.9(4)	24.9(4)
Si(2)	53.8(5)	69.3(6)	48.4(5)	24.8(4)	19.2(4)	33.1(5)
O(1)	55(1)	65(1)	49(1)	21(1)	21(1)	29(1)
N(1)	52(1)	59(2)	47(1)	21(1)	20(1)	28(1)
C(1)	55(2)	55(2)	58(2)	23(2)	23(2)	28(2)
C(2)	66(2)	63(2)	59(2)	24(2)	26(2)	30(2)
C(3)	90(3)	99(3)	69(2)	45(2)	45(2)	55(3)
C(4)	79(3)	101(3)	118(4)	66(3)	61(3)	45(3)
C(5)	58(2)	74(3)	124(4)	37(3)	39(3)	22(2)
C(6)	56(2)	69(2)	75(2)	18(2)	20(2)	24(2)
C(7)	75(2)	76(2)	66(2)	23(2)	30(2)	46(2)
C(8)	75(2)	55(2)	83(3)	23(2)	22(2)	17(2)
C(9)	63(2)	118(3)	60(2)	17(2)	12(2)	39(2)
C(10)	98(3)	97(3)	90(3)	59(2)	52(2)	64(3)
F(2)	85(1)	78(1)	62(1)	10(1)	28(1)	21(1)
F(3)	138(2)	156(2)	77(2)	54(2)	66(2)	74(2)
F(4)	123(2)	169(3)	177(3)	111(2)	107(2)	64(2)
F(5)	71(2)	110(2)	194(3)	38(2)	55(2)	1(2)
F(6)	67(1)	97(2)	90(2)	—3(1)	14(1)	14(1)
Si(3)	43.7(4)	51.0(5)	47.9(5)	21.8(4)	17.7(4)	16.0(4)
Si(4)	41.0(5)	88.4(7)	61.0(6)	46.8(5)	22.2(4)	28.8(5)
O(2)	49(1)	66(1)	49(1)	31(1)	21(1)	26(1)
N(2)	42(1)	60(2)	45(1)	27(1)	18(1)	21(1)
C(11)	44(2)	58(2)	48(2)	26(1)	15(1)	16(1)
C(12)	65(2)	68(2)	55(2)	27(2)	22(2)	27(2)
C(13)	77(2)	78(3)	53(2)	15(2)	24(2)	20(2)
C(14)	74(2)	102(3)	44(2)	29(2)	15(2)	19(2)
C(15)	67(2)	94(3)	59(2)	47(2)	15(2)	28(2)
C(16)	62(2)	69(2)	58(2)	33(2)	22(2)	28(2)
C(17)	80(3)	67(2)	81(3)	2(2)	19(2)	25(2)
C(18)	54(2)	97(3)	89(3)	62(2)	32(2)	25(2)
C(19)	53(2)	170(5)	78(3)	68(3)	3(2)	—8(3)
C(20)	120(4)	160(5)	153(4)	113(4)	101(4)	108(4)
F(12)	118(2)	87(2)	72(1)	34(1)	40(1)	63(1)
F(13)	129(2)	111(2)	67(1)	8(1)	41(1)	46(2)
F(14)	128(2)	161(3)	46(1)	39(1)	20(1)	43(2)
F(15)	119(2)	143(2)	85(2)	77(2)	26(1)	67(2)
F(16)	110(2)	96(2)	81(1)	50(1)	40(1)	66(1)

Crystals suitable for X-ray crystallography were obtained by recrystallisation from hexane (m.p. 108—110°C); that used for data collection was sealed in a thin walled capillary.

Preliminary cell parameters were obtained from oscillation and Weissenberg photographs and refined on a Hilger and Watts four circle diffractometer. Data were collected for 3946 reflections of which 3928 had $I > 3\sigma(I)$. The structure was solved by direct methods (MULTAN) [15] and refined by conventional least squares and Fourier methods (CRYSTALS) [16]. Refinement converged at R 14.6% with isotropic and R 5.6% with anisotropic thermal parameters. A difference Fourier synthesis revealed the positions of all 24 hydrogen atoms but these were inserted at their calculated positions and not refined in subsequent cycles. Final convergence occurred at R 3.9% with unit weighting. Final atomic coordinates are listed in Table 1 and anisotropic thermal parameters in Table 2. Observed and calculated structure factors are available from the authors (D.B.S.).

Discussion

The asymmetric unit contains two half molecules which lie on crystallographic centres. The diagram in Fig. 1 shows the molecular structure and atom numbering scheme for the Si(1)—O(1)—Si(2)—N(1) molecule; that in the Si(3)—O(2)—Si(4)—N(2) molecule is similar. The relative orientation of the two molecules in the unit cell is shown in Fig. 2, the molecules are projected onto the b c plane and for clarity the methyl groups and the C_6F_5 groups, with the exception of carbon atom attached to nitrogen, have been omitted. Important bond lengths and angles are collected in Table 3; the dimensions of the C_6F_5 groups are normal (mean C—C 1.372, mean C—F 1.339 Å, mean C—C—C 120.0, mean C—C—F 119.5°), except that the ring angles at C(1) and C(11) are reduced to 115.7 and 115.4° respectively.

A major feature of each ring is the distorted chair conformation which arises from the presence of a crystallographic centre of symmetry. In each case, the four silicon atoms are coplanar with the nitrogen and oxygen atoms being displaced on average 0.62 and 0.45 Å respectively from the appropriate plane. Details of this plane and the best plane through all the ring atoms are given in Table 4. In the C_6F_5 groups, no atom deviates by >0.02 Å from the mean plane.

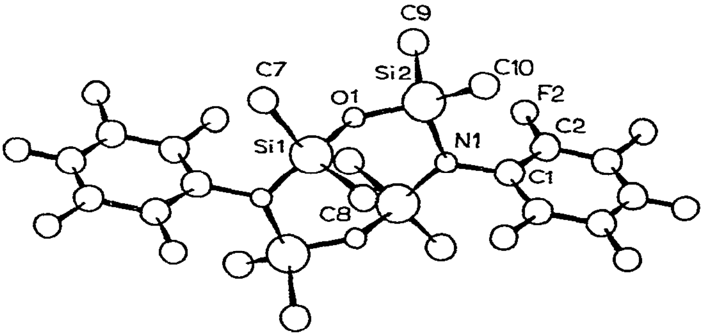


Fig. 1. Molecular structure and atom numbering scheme for molecule 1.

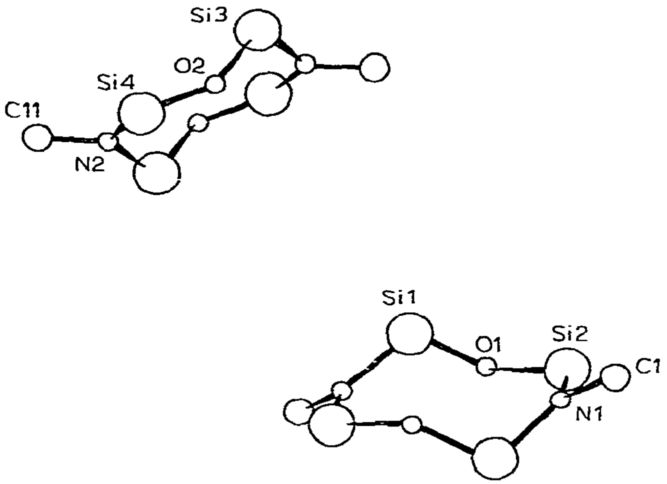


Fig. 2. Relative orientations of the two silazoxane rings (projection onto the *bc* plane).

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (deg)

Molecule 1		Molecule 2	
Si(1)—O(1)	1.629(2)	Si(3)—O(2)	1.625(2)
Si(1)—N(1′)[a]	1.746(2)	Si(3)—N(2″)[b]	1.742(2)
Si(1)—C(7)	1.848(3)	Si(3)—C(17)	1.842(4)
Si(1)—C(8)	1.846(3)	Si(3)—C(18)	1.838(3)
Si(2)—O(1)	1.619(2)	Si(4)—O(2)	1.618(2)
Si(2)—N(1)	1.750(2)	Si(4)—N(2)	1.748(2)
Si(2)—C(9)	1.845(4)	Si(4)—C(19)	1.837(4)
Si(2)—C(10)	1.847(4)	Si(4)—C(20)	1.846(4)
N(1)—C(1)	1.413(4)	N(2)—C(11)	1.416(3)
O(1)—Si(1)—N(1′)	109.2(1)	O(2)—Si(3)—N(2″)	109.9(1)
O(1)—Si(1)—C(7)	107.9(1)	O(2)—Si(3)—C(17)	108.6(1)
O(1)—Si(1)—C(8)	109.7(1)	O(2)—Si(3)—C(18)	109.0(1)
N(1′)—Si(1)—C(7)	108.8(1)	N(2″)—Si(3)—C(17)	109.1(1)
N(1′)—Si(1)—C(8)	109.2(1)	N(2″)—Si(3)—C(18)	108.9(1)
C(1)—Si(1)—C(8)	112.1(2)	C(17)—Si(3)—C(18)	111.2(2)
O(1)—Si(2)—N(1)	106.1(1)	O(2)—Si(4)—N(2)	106.4(1)
O(1)—Si(2)—C(9)	106.7(1)	O(2)—Si(4)—C(19)	111.6(2)
O(1)—Si(2)—C(10)	112.0(1)	O(2)—Si(4)—C(20)	106.7(2)
N(1)—Si(2)—C(9)	112.7(1)	N(2)—Si(4)—C(19)	108.6(2)
N(1)—Si(2)—C(10)	108.5(1)	N(2)—Si(4)—C(20)	112.5(2)
C(9)—Si(2)—C(10)	110.7(2)	C(19)—Si(4)—C(20)	111.0(3)
Si(1)—O(1)—Si(2)	147.3(1)	Si(3)—O(2)—Si(4)	148.0(1)
Si(1′)—N(1)—Si(2)	123.3(1)	Si(3″)—N(2)—Si(4)	123.0(1)
Si(1′)—N(1)—C(1)	118.8(2)	Si(3″)—N(2)—C(11)	118.6(2)
Si(2)—N(1)—C(1)	117.9(2)	Si(4)—N(2)—C(11)	118.4(2)
N(1)—C(1)—C(2)	121.9(3)	N(2)—C(11)—C(12)	122.2(3)
N(1)—C(1)—C(6)	122.4(3)	N(2)—C(11)—C(16)	122.4(3)

[a] Atoms carrying a prime are related to unprimed atoms by the symmetry operation $x, y, z \rightarrow 1-x, \bar{y}, 1-z$.
[b] Atoms carrying a double prime are related to unprimed atoms by the symmetry operation $x, y, z \rightarrow 1-x, 1-y, 2-z$.

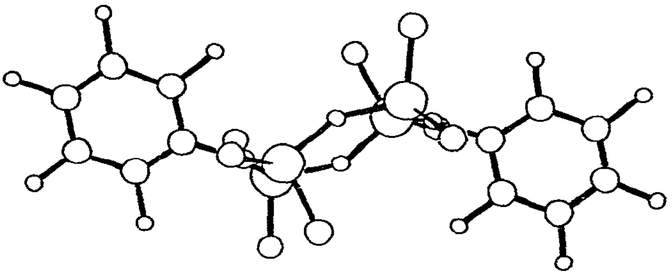
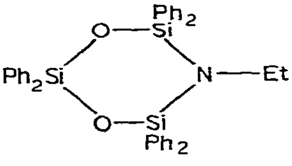


Fig. 3. Molecular structure of molecule 2, showing the orientation of the C_6F_5 groups.

Figure 3 shows that the pentafluorophenyl groups are almost perpendicular to the mean plane of the silazoxane ring and this is confirmed by values of 82.7 and −108.2° respectively, for the Si(1)—N(1)—C(1)—C(6) and Si(3)—N(2)—C(11)—C(16) torsion angles.

Mean values for the Si—N and Si—O distances are 1.747 and 1.623 Å respectively, and are similar to those formed in *N*-ethyl-hexaphenyl-3-azacyclosiloxane (**2**) [11] and tetramethyl-tetraphenyl-tetrasila-2,6-diaza-4,8-dioxane (**3**) [12].

The Si—O—Si angle varies substantially in different cyclic structures but the value here, 147.7°, is comparable to that, 148.5°, found for compound **3**. The Si—N—Si angle (123.2°) is only slightly greater than that expected for sp^2 hybridisation but it is substantially smaller than that for **3** (130°) or for those observed in octamethylcyclotetrasilazane (130.1 to 133.1°) [6]. The O—Si—N angles fall into two groups, 106.2 and 109.6°, but the average of the six angles at each silicon atom is 109.47°. It is unlikely that these differences are caused by either intra- or inter-molecular contacts between the methyl hydrogen atoms and the ring oxygen or nitrogen atoms as these are evenly distributed in the range 2.95—3.15 Å. Perhaps the most significant intermolecular interactions are those between fluorine atoms of the C_6F_5 groups and hydrogen atoms. In each molecule there are 31 of these at distances $\leqslant 3.5$ Å; 13 occur at <3.0 Å although only one, that between F(2) and HC(17) (2.64 Å), is at the sum of the Van der Waals' radii. Somewhat surprisingly, neither N···H nor O···H intermolecular interactions are important, there being only one O···H contact (3.31 Å) at less than 3.5 Å.



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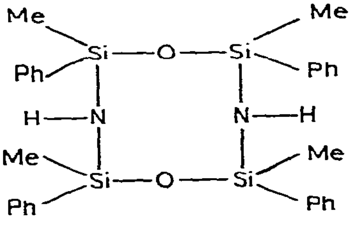

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TABLE 4

EQUATIONS OF MEAN PLANES AND DISTANCES (Å) OF RELEVANT ATOMS FROM THE PLANE

Plane 1	Si(1), N(1), O(1), *Si*(2) $-4.125x + 9.641y + 1.777z = -1.174$ Si(1) — 0.382, Si(2) 0.053, N(1) —0.296, O(1) 0.286, C(7) 0.054, C(8) —2.208, C(9) 1.612, C(10) —1.383, C(1) —1.173
Plane 2	Si(1), Si(2), Si(1′), Si(2′) $5.381x + 8.134y - 3.296z = 1.042$ N(1) 0.612, O(1) —0.457
Plane 3	Si(3), N(2), O(2), *Si*(4) $-2.214x + 9.681y + 7.164z = 10.898$ *Si*(3) 0.383, *Si*(4) —0.061, N(2) 0.303, O(2) —0.274, C(17) 2.198, C(18) 0.019, C(19) 1.351, C(20) —1.638, C(11) 1.223

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