Journal of Organometallic Chemistry, 310 (1986) 161–167
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CRYSTAL STRUCTURE OF BIS(*N*-PENTAFLUOROPHENYL)-TETRAPHENYL-CYCLODISILAZANE-TETRABENZENE, $(Ph_2SiNC_6F_5)_2 \cdot 4C_6H_6$

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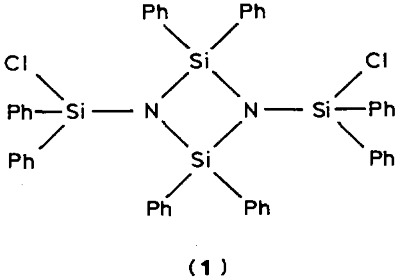
(Received March 6th, 1986)

Summary

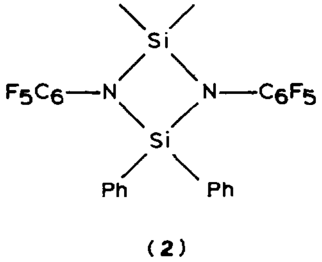
The disilazane $(Ph_2SiNC_6F_5)_2$ crystallises from benzene solution with four molecules of solvent in the orthorhombic space group *Pnna* with *a* 18.182(6), *b* 21.480(8) and *c* 13.631(5) Å, $Z = 4$. The structure was solved by direct methods and refined by least-squares to *R* 0.069 for 937 observed reflections. The Si_2N_2 ring is planar with N–Si–N and Si–N–Si angles of 85.2 and 95.5° respectively; the mean Si–N distance is 1.755 Å. The C_6F_5 groups are twisted by ca. 16° from the Si_2N_2 plane and the benzene molecules are arranged face-on above and below each of the C_6F_5 groups. There are, in addition, short intermolecular contacts between four fluorines of each C_6F_5 group and hydrogen atoms from both solvate benzene and the phenyl groups of a symmetry related silazane. Attempts to refine the related $(Me_2SiNC_6F_5)_2$ structure were not successful, probably due to disorder.

Introduction

A number of disilazane structures have been determined previously [1–7], and show Si–N bond distances between 1.72 and 1.76 Å; the N–Si–N angles fall between 85.1 and 89.4° and the Si–N–Si angles between 90.5 and 94.9°. One of these compounds, bis(*N*-chlorodiphenylsilyl)-tetraphenyl-cyclodisilazane (**1**) [5], crystallises as a 1 : 1 benzene solvate, but no data were given for the non-bonding interactions between the benzene molecule and the disilazane. The *N*-pentafluoro-



(**1**)



(**2**)

0022-328X/86/$03.50

phenyl-substituted disilazane (**2**) crystallises as a tetrabenzene solvate, and we have determined its structure in order to elucidate the nature of the silazane–benzene interactions.

Structure determination

The compound was prepared as described previously [8], and crystals suitable for X-ray analysis were obtained from benzene. However, the crystals became cloudy

TABLE 1

ATOMIC COORDINATES ($\times 10^3$) (with estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c
Si(1)	632.3(2)	249.5(3)	154.5(3)
N(1)	566(1)	250	250
N(2)	697(1)	250	250
C(21)	490(1)	250	250
C(22)	450(1)	236(1)	167(2)
C(23)	375(1)	234(1)	167(1)
C(24)	340(1)	250	250
F(22)	485.0(5)	219.1(5)	87(1)
F(23)	337.8(6)	218.2(6)	88(1)
F(24)	263(1)	250	250
C(31)	771(2)	250	250
C(34)	932(2)	250	250
C(35)	890(1)	234(1)	330(2)
C(36)	813.0(7)	235(1)	328(1)
F(34)	1003(1)	250	250
F(35)	925.2(5)	219.5(6)	415(1)
F(36)	779.5(5)	221.2(5)	415(1)
C(1)	638(1)	177(1)	79(2)
C(2)	671(1)	173(1)	−12(2)
C(3)	677(1)	116(1)	−63(2)
C(4)	645(1)	64(1)	−17(2)
C(5)	612(1)	66(1)	70(2)
C(6)	611(1)	123(1)	119(1)
C(7)	627(1)	320(1)	83(2)
C(8)	594(1)	318(1)	−10(1)
C(9)	590(1)	369(1)	−73(2)
C(10)	614(1)	423(1)	−40(2)
C(11)	650(1)	431(1)	50(2)
C(12)	657(1)	376(1)	112(1)
C(41)	847(1)	73(1)	245(2)
C(42)	825(1)	93(1)	154(2)
C(43)	876(1)	110(1)	92(2)
C(44)	949(1)	105(1)	102(2)
C(45)	971(1)	83(1)	196(2)
C(46)	922(1)	67(1)	265(2)
C(51)	299(1)	89(1)	333(2)
C(52)	332(1)	66(1)	247(3)
C(53)	407(2)	62(1)	242(3)
C(54)	445(1)	82(1)	315(2)
C(55)	414(1)	102(1)	407(2)
C(56)	336(1)	105(1)	408(2)

after ca. 1 h in the open laboratory, and were completely opaque after 12 h. Oscillation photographs confirmed the loss of long range order in these crystals, and for data collection a crystal was sealed with a drop of a saturated benzene solution in a thin walled Lindemann tube.

Crystal data. $[(C_6H_5)_2SiNC_6F_5]_2 \cdot 4C_6H_6$, $C_{60}H_{44}F_{10}N_2Si_2$, $M = 1039.2$, orthorhombic, a 18.182(6), b 21.480(8), c 13.631(5) Å, U 5323.6 Å^3, $Z = 4$, D_m ca. 1.4 , D_c 1.30 g cm^{-3}, $F(000) = 2144$, space group *Pnna*, μ 15.4 cm^{-1}, Cu-K_α radiation, λ 1.5418 Å.

The structure was solved by direct methods (MULTAN 78) [9] and refined by full matrix, least-squares (CRYSTALS) [10] using 937 independent reflections for which $I > 3\sigma(I)$. The data were corrected for Lorentz and polarisation effects; scattering factors were for neutral atoms [11]. The asymmetric unit consists of one half the molecular unit; a two-fold axis passes through the nitrogen atoms of the silazane ring and the two C_6F_5 groups. Two molecules of benzene are also included in the asymmetric unit. The refinement converged at R 0.112 with isotropic and at R 0.069 with anisotropic thermal parameters for the atoms in the $Si(NC_4F_3)_2$ unit; the hydrogen atoms were placed (but not refined) as their calculated positions. The final atomic coordinates are listed in Table 1. Tables of calculated hydrogen atom positions, thermal parameters, and observed and calculated structure factors are available from the authors.

The dimethyl analogue, $(Me_2SiNC_6F_5)_2$, was not solvated on crystallisation from benzene but preliminary photographs showed that all crystals were twinned. The unit cell dimensions were determined (a 17.26, b 7.12, c 8.72 Å and β 120.16°) and the systematic absences indicated a C-centred cell. From the measured density (1.7 g cm^{-3}) the unit cell contains two molecular units. Initially, solution was attempted in the space group *C*2, but similar, poor, solutions were obtained in both *Cm* and *C*2/*m*. The MULTAN solution with the highest combined figure of merit was interpreted in terms of two silicon atoms lying on a two-fold axis, one unique nitrogen atom, and one methyl carbon atom. Using these positions to phase a difference Fourier synthesis (CRYSTALS) gave atoms consisting of an incomplete and highly distorted C_6F_5 group. Refinement showed poor convergence at R 0.22 with isotropic thermal parameters, which was reduced to R 0.19 with anisotropic parameters. The structure, which is apparently very similar to that of the phenyl derivative, shows the following parameters: Si–N 1.72, 1.85 Å; N–Si–N 85.5; Si–N–Si 93.8°.

Discussion

Important bond distances and angles for **2** are listed in Table 2, and a projection of the molecule onto the Si_2N_2 plane, which also shows the atom numbering scheme, is shown in Fig. 1. The carbon atoms of the two independent benzene molecules of solvation are numbered C(41)–C(46) and C(51)–C(56), respectively.

The mean Si–N bond length (1.755 Å) is at the upper end of the range (1.72–1.76 Å) previously observed [1–7], and the N(1)–Si(1)–N(2) angle (84.4°) is even more acute than that in $(Me_2SiNC_6H_3Me_2)_2$ (85.1°) [6], until now the smallest known angle. There is a corresponding increase to 113.5° in the C(1)–Si(1)–C(7) angle, giving a very distorted tetrahedral coordination about silicon. The Si–N–Si angles

TABLE 2

IMPORTANT BOND LENGTHS (Å) AND ANGLES (°) (with estimated standard deviations in parentheses)

Si(1)-N(1)	1.76(1)
Si(1)-N(2)	1.75(1)
Si(1)-C(1)	1.87(2)
Si(1)-C(7)	1.81(2)
N(1)-C(21)	1.40(2)
N(2)-C(31)	1.35(3)
N(1)-Si(1)-N(2)	84.4(5)
N(1)-Si(1)-C(1)	117.0(7)
N(1)-Si(1)-C(7)	111.1(7)
N(2)-Si(1)-C(1)	112.3(7)
N(2)-Si(1)-C(7)	115.5(7)
C(1)-Si(1)-C(7)	113.5(6)
Si(1)-N(1)-Si(1′) [a]	95.2(8)
Si(1)-N(1)-C(21)	132.4(4)
Si(1)-N(2)-Si(1′)	95.9(9)
Si(1)-N(2)-C(31)	132.0(5)
Si(1)-C(1)-C(6)	117.0(16)
Si(1)-C(1)-C(2)	125.1(16)
Si(1)-C(7)-C(12)	123.7(17)
Si(1)-C(7)-C(8)	119.2(15)

[a] Atoms carrying a prime are related by the symmetry operation $x, \frac{1}{2} - y, \frac{1}{2} - z$.

(mean 95.6°), on the other hand, are the largest observed in a cyclodisilazane, and probably result from a reduction in the antibonding interaction between the *trans* nitrogen atoms. This is favoured by the electron-withdrawing properties of the C_6F_5 group and is in agreement with a recent molecular orbital treatment of the Si_2N_2 ring system [12].

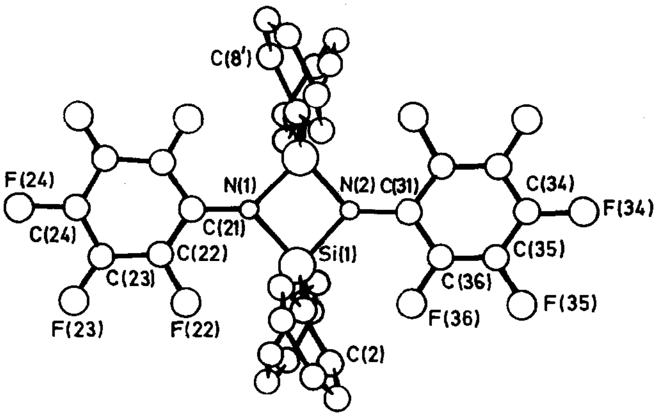


Fig. 1. Projection of the molecule onto the plane of the Si_2N_2 ring showing the atom numbering scheme.

TABLE 3

TORSION ANGLES (°)

Si(1)–N(1)–C(21)–C(22)	13.9
Si(1)–N(2)–C(31)–C(36)	−162.2
N(1)–Si(1)–C(1)–C(2)	162.8
N(1)–Si(1)–C(7)–C(8)	−104.7
C(1)–Si(1)–N(1)–C(21)	−67.2
C(7)–Si(1)–N(1)–C(21)	65.2
C(7)–Si(1)–C(1)–C(2)	31.5
C(1)–Si(1)–C(7)–C(8)	29.9

Bond lengths and angles within the three types of aromatic ring show substantial variations, especially in the solvate benzene molecules where the C–C distances range between 1.28 and 1.44 Å (mean 1.36 Å) and the C–C–C angles between 114 and 128° (mean 120°). Mean C–C distances in the phenyl and C_6F_5 groups are 1.39 and 1.37 Å, respectively, with mean C–C–C angles of 120.0 and 119.2°, respectively. The mean C–F distance is 1.34 Å and the C–C–F angles have a mean value of 119.2°.

The Si_2N_2 ring is planar, with the two carbon atoms of the attached C_6F_5 groups also in the plane; torsion angles of 13.9 and −162.2° for the Si(1)–N(1)–C(21)–C(22) and Si(1)–N(2)–C(31)–C(36) angles indicate that the planes of the C_6F_5 groups

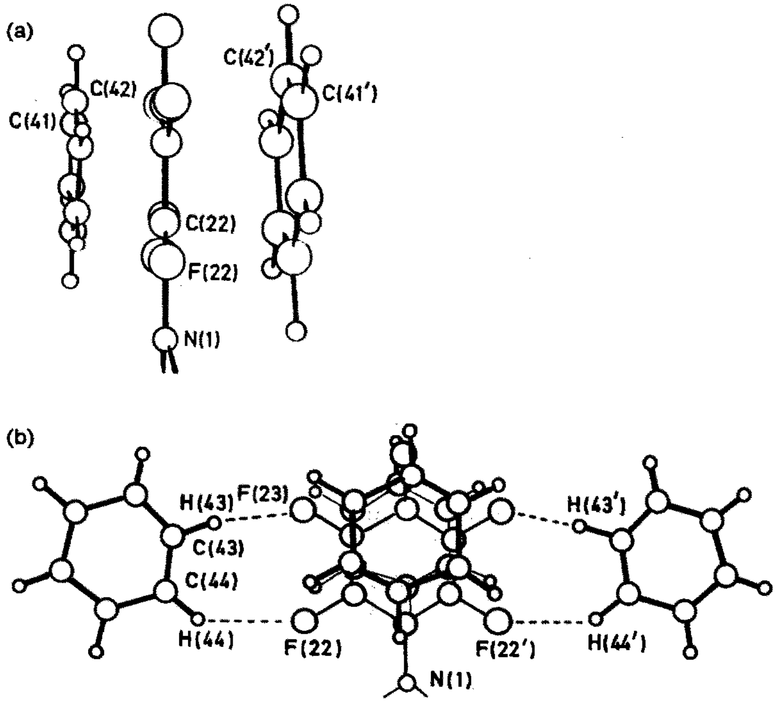


Fig. 2. (a) Orientation of the C(41) benzene molecules with respect to the N(1)–C_6F_5 group; (b) Intermolecular H···F interactions between solvate benzene and the N(1)–C_6F_5 group. (The C(41) benzene molecules above and below the C_6F_5 group are shown in, respectively, thick and thin lines.)

TABLE 4

INTERMOLECULAR CONTACTS (< 3.8 Å) BETWEEN THE BENZENE ATOMS AND CARBON ATOMS OF THE C_6F_5 GROUPS

C(21)–C(54) [a]	3.80
C(22)–C(55′) [b]	3.69
C(23)–C(55′)	3.73
C(23)–C(56′)	3.67
C(24)–C(51) [a]	3.71
C(24)–C(56) [a]	3.79
C(31)–C(42) [a]	3.74
C(34)–C(44) [a]	3.73
C(34)–C(45) [a]	3.73
C(35)–C(41)	3.74
C(35)–C(43′)	3.53
C(35)–C(44′)	3.73
C(35)–C(46)	3.74
C(36)–C(41)	3.72
C(36)–C(42) [a]	3.69
C(36)–C(43)	3.69

[a] Contact also to an equivalent atom related by the symmetry operation x, $\frac{1}{2}-y$, $\frac{1}{2}-z$. [b] Atoms carrying a prime are related to unprimed atoms by the symmetry operation x, $\frac{1}{2}-y$, $\frac{1}{2}-z$.

deviate only slightly (ca. 16°) from the Si_2N_2 plane. The carbon atoms of the phenyl group attached to silicon are displaced by 1.53 Å above and below the Si_2N_2 plane. Atoms in the C_6F_5, C_6H_5 and C_6H_6 groups are planar; the deviation of any atom from the best plane through the appropriate atoms is < 0.03 Å. Torsion angles giving the orientation of the C_6F_5 and C_6H_5 groups are collected in Table 3.

The most interesting aspect of the structure is the presence of sixteen molecules of solvate benzene in the unit cell, i.e. four molecules per silazane molecule. A number of similarly heavily solvated species are known, including $Si_6Ph_{12} \cdot 7PhH$ [13], $Ge_6Ph_{12} \cdot 2PhH$ [14] and $Ge_6Ph_{12} \cdot 7PhH$ [14]. In the present compound the benzene molecules are arranged above and below each pentafluorophenyl group and

TABLE 5

OTHER CLOSE INTERMOLECULAR CONTACTS

F(22)–H(44′) [a]	2.89
F(23)–H(43′) [a]	2.55
F(35)–H(55′) [b]	2.77
F(36)–H(56′) [b]	2.72
F(23)–H(2′) [a]	2.77
F(35)–H(8′) [c]	2.81
F(36)–H(2′) [d]	2.81
C(22)–F(35′) [e]	3.59
C(23)–F(35′) [e]	3.69
C(35)–F(23′) [c]	3.78
C(36)–F(23′) [c]	3.71

[a] Related by the symmetry operation $x-\frac{1}{2}$, y, $-z$. [b] Related by the symmetry operation $\frac{1}{2}+x$, y, $1-z$. [c] Related by the symmetry operation $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$. [d] Related by the symmetry operation x, $\frac{1}{2}-y$, $\frac{1}{2}-z$. [e] Related by the symmetry operation $x-\frac{1}{2}$, $\frac{1}{2}-y$, z-$\frac{1}{2}$.

show two types of intermolecular interactions. The first is effectively 'face on', see Fig. 2(a), where the planes of the C_6F_5 and C_6H_6 groups are separated by ca. 3.7 Å; Pauling's estimate [15] of the half thickness of an aromatic group is 1.7 Å. The closest $C \cdots C$ intermolecular contacts ($<$ 3.8 Å) are listed in Table 4. The second type of interaction, see Fig. 2(b), involves four fluorine atoms of each C_6F_5 group [F(22), F(23), F(35), F(36) and their symmetry related pairs] and hydrogen atoms of the benzene molecules. The $F \cdots H$ separations, at the limit of the sum of the hydrogen and fluorine Van der Waals radii (2.6 Å) are given in Table 5. This table also includes a number of other short intermolecular contacts, principally between the C_6F_5 groups and both phenyl groups attached to silicon.

References

1 P.J. Wheatley, J. Chem. Soc., (1962) 1721.
2 G. Chioccola and J.J. Daly, J. Chem. Soc. A, (1968) 1658.
3 D. Mootz, J. Fayos and A. Zinnius, Angew. Chem. Int. Ed. Engl., 11 (1972) 58.
4 L. Parkanyi, G.Y. Argay, P. Hencsei and J. Nagy, J. Organomet. Chem., 116 (1976) 299.
5 S.N. Gurkova, A.I. Gusev, N.V. Alekseev, Yu. M. Varezhkin, M.M. Morgunova and D.Ya. Zhinkin, J. Struct. Chem., 19 (1978) 164.
6 W. Clegg, U. Klingebiel, G.M. Sheldrick and N. Vater, Z. Anorg. Allg. Chem., 482 (1981) 88.
7 W. Clegg, M. Hesse, U. Klingebiel, G.M. Sheldrick and L. Skoda, Z. Naturforsch. B, 35 (1980) 1359.
8 I. Haiduc and H. Gilman, Synth. Inorg. Metal-Org. Chem., 1 (1971) 75.
9 G. Germain, P. Main and M.M. Woolfson, Acta Cryst., A27 (1971) 368.
10 J.R. Carruthers, CRYSTALS, the Oxford Crystallographic Programs, (1975).
11 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, (1974) Vol. 4.
12 I. Silaghi-Dumitrescu and I. Haiduc, Inorg. Chim. Acta, 112 (1986) 159.
13 M. Dräger and K.G. Walter, Z. Anorg. Allg. Chem., 479 (1981) 65.
14 M. Dräger, L. Ross and D. Simon, Z. Anorg. Allg. Chem., 466 (1980) 145.
15 L. Pauling, The Nature of the Chemical Bond, 3rd ed., 1960, p. 260.