

## CRYSTAL AND MOLECULAR STRUCTURE OF TETRAMETHYL-*N,N'*-DIPHENYLCYCLODISILAZANE

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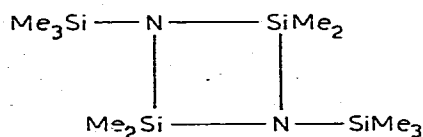
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### Summary

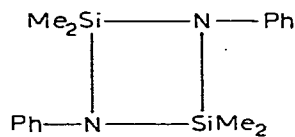
The crystal structure of tetramethyl-*N,N'*-diphenylcyclodisilazane is reported. The molecule has a centre of symmetry and the phenyl groups are almost coplanar with the cyclodisilazane ring. Si—N bond distances are 1.739(3) and 1.749(3) Å, the mean Si—C bond length is 1.849 and the C—N bond length is 1.382(4) Å, while the N—Si—N and Si—N—Si bond angles are 85.7(1) and 94.3(1)° respectively. Considerable bathochromic shifts are found in the UV spectra of the compound compared with that of *N*-phenyl(hexamethyl)disilazane. Structural and spectroscopic data show enhanced delocalization. The  $\pi$ -bond orders calculated by the PPP method are  $p(\text{C—N})$  0.325 and  $p(\text{Si—N})$  0.346.

### Introduction

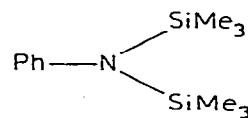
The crystal structure of tetramethyl-*N,N'*-bis(trimethylsilyl)cyclodisilazane (I) was determined by Wheatley [1] and was refined using two-dimensional data. The three valencies of the nitrogen atoms are coplanar and the Si—N bond lengths (1.70, 1.72 and 1.73 Å) are shorter than the sum of the covalent radii of silicon



(I)



(II)



(III)

and nitrogen (1.80 Å) corrected for the electronegativity difference. Thus there

is some delocalization of the nitrogen lone pair, as is usual for silazanes (e.g. [2]).

The aim of the present study is to obtain accurate structural data for compound II (and the cyclodisilazane ring in general) and to investigate the effect of the phenyl groups on the delocalization.

## Experimental

### Determination of the crystal structure

**Crystal data:**  $C_{16}H_{22}N_2Si_2$ , mol. wt. 298.54,  $a$  8.545(2),  $b$  16.820(3),  $c$  11.622(2) Å,  $V$  1670.38 Å<sup>3</sup>,  $Z = 4$ ,  $D_x$  1.187 g cm<sup>-3</sup>,  $F(000)$  640, space group  $Pbca$  (No. 61),  $\mu$  for Cu- $K\alpha$  ( $\lambda$  1.5418 Å) 18.22 cm<sup>-1</sup>. Unit cell dimensions were determined from zero-layer precession photographs. 1253 intensities were collected on a Stoe two-circle semi-automatic diffractometer in the equi-inclination arrangement for the  $0kl \rightarrow 7kl$  layers by the  $\omega$ -scanning method with Cu- $K\alpha$  radiation and a scintillation counter (Ni-filter and pulse-height discriminator). 173 reflexions of the data set with  $I - 1.5 \sigma(I) \leq 0$  were taken as unobserved with the value of  $I_0 = 0.5 \sigma(I)$ . After data reduction an absolute scale factor and overall temperature factor ( $B$  4.7 Å<sup>2</sup>) 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]. The  $R$ -value for the trial structure was 0.22 ( $R = \sum \| |F_o| - |F_c| \| / \sum |F_o|$ ). Atomic coordinates were then refined using the program of Albano et al. [4]. The function minimized was  $\Phi = w \times (|F_o| - 1/G|F_c|)^2$ , where  $w$  is the weighting scheme of Cruickshank et al. [5], and  $G$  is the scaling factor [ $w = (3.0 + 1.0 F_o + 0.008 F_o^2)^{-1}$ ]. After four cycles isotropic and two cycles anisotropic full-matrix least-squares refinement ( $R = 0.089$ ), the five hydrogen atomic positions of the phenyl ring were geometrically generated, and a difference-Fourier map was computed in which the six methyl hydrogen atoms were located. A further six cycles of anisotropic refinement of the non-hydrogen atoms were then performed and in the last three cycles the hydrogen atoms were refined isotropically. The final  $R$  value was 0.058 for the

TABLE I

THE FINAL ATOMIC PARAMETERS ( $\times 10^4$ ) WITH THEIR e.s.d.'s IN PARENTHESES. ANISOTROPIC THERMAL PARAMETERS ARE GIVEN IN THE FORM:

$$T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$$

Atom	$x/a$	$y/b$	$z/c$	$b_{11}$	$b_{12}$	$b_{13}$	$b_{22}$	$b_{23}$	$b_{33}$
Si	3947(1)	-135(1)	5758(1)	116(2)	8(1)	30(1)	32(1)	6(1)	54(1)
N	4314(4)	579(2)	4709(2)	124(4)	13(3)	42(5)	33(1)	16(2)	70(2)
C(1)	2147(5)	-715(3)	5506(3)	143(6)	-19(5)	21(7)	49(2)	0(4)	90(3)
C(2)	3997(5)	242(3)	7255(3)	217(8)	8(6)	17(7)	52(2)	-19(4)	62(3)
C(3)	3490(4)	1238(2)	4337(3)	111(5)	9(4)	-16(6)	31(1)	-17(3)	67(2)
C(4)	3965(4)	1671(2)	3387(3)	150(6)	-3(4)	-17(6)	37(1)	8(3)	79(3)
C(5)	3130(5)	2329(2)	3022(4)	196(7)	2(5)	-51(8)	33(1)	12(4)	109(3)
C(6)	1816(5)	2560(2)	3590(4)	209(7)	25(5)	-99(9)	31(1)	-7(4)	143(4)
C(7)	1306(5)	2143(2)	4519(4)	159(7)	43(5)	-11(9)	40(1)	-34(4)	141(4)
C(8)	2138(5)	1479(2)	4894(4)	160(6)	21(5)	33(7)	39(1)	-12(4)	95(3)

TABLE 2

FRACTIONAL COORDINATES ( $\times 10^3$ ), ISOTROPIC TEMPERATURE PARAMETERS ( $\text{\AA}^2$ ) AND BOND DISTANCES ( $\text{\AA}$ ) FOR THE HYDROGEN ATOMS

Atom	$x/a$	$y/b$	$z/c$	$B$	C—H
H(11)	220(6)	-120(3)	598(4)	5.5(1.3)	0.99(5)
H(12)	230(7)	-96(3)	481(5)	7.3(1.5)	0.93(6)
H(13)	110(6)	-42(3)	568(4)	4.4(1.2)	1.03(5)
H(21)	487(6)	50(3)	754(4)	5.4(1.1)	0.93(5)
H(22)	331(5)	64(3)	739(4)	5.2(1.1)	0.90(5)
H(23)	398(6)	-15(3)	777(4)	4.2(1.2)	0.90(5)
H(4)	501(5)	152(2)	300(4)	4.1(1.0)	1.03(4)
H(5)	352(5)	268(3)	231(4)	4.4(1.1)	1.07(5)
H(6)	120(5)	306(3)	346(4)	4.4(1.1)	1.00(5)
H(7)	43(6)	227(3)	500(4)	4.5(1.1)	0.96(5)
H(8)	179(6)	117(3)	554(4)	4.7(1.2)	0.96(5)

TABLE 3

UV MAXIMA

Compound	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$	Solvent
II [This work]	258	45000	n-Heptane
	282	3940	
	287	3900	
	299	2490	
III [7]	235	3980	Cyclohexane
	266	470	
	272	450	
	298(sh)	100	

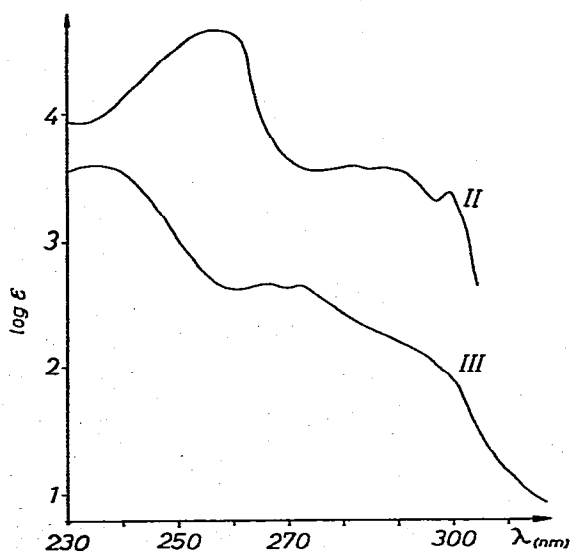


Fig. 1. Ultraviolet spectra of compounds II and III.

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) FOR THE NON-HYDROGEN ATOMS WITH THEIR e.s.d.'s IN PARENTHESES

Bond lengths					
Si—C(1)	1.845(4)	N—C(3)	1.382(4)	C(6)—C(7)	1.359(6)
Si—C(2)	1.852(4)	C(3)—C(4)	1.384(5)	C(7)—C(8)	1.393(6)
Si—N	1.739(3)	C(4)—C(5)	1.384(6)	C(8)—C(3)	1.385(5)
Si—N'	1.749(3)	C(5)—C(6)	1.360(6)		
Bond angles					
C(1)—Si—C(2)	110.4(2)	N'—Si—N	85.7(1)	N—C(3)—C(8)	120.9(3)
C(1)—Si—N	113.9(2)	Si—N—Si'	94.3(1)	C(8)—C(3)—C(4)	117.6(3)
C(1)—Si—N'	115.6(2)	Si—N—C(3)	132.9(2)	C(3)—C(4)—C(5)	121.0(3)
C(2)—Si—N	114.7(2)	Si'—N—C(3)	132.7(2)	C(4)—C(5)—C(6)	120.4(4)
C(2)—Si—N'	114.7(2)	N—C(3)—C(4)	121.5(3)	C(5)—C(6)—C(7)	120.2(4)
		C(6)—C(7)—C(8)	119.9(4)		
		C(7)—C(8)—C(3)	121.0(4)		

observed, and 0.076 for all reflexions\*.

The atomic parameters for the non-hydrogen atoms are given in Table 1 and hydrogen atomic coordinates, isotropic temperature factors and C—H distances in Table 2. Atomic scattering factors were taken from International Tables for X-ray Crystallography [6].

#### UV spectroscopic investigations

The UV spectrum of the title compound was recorded in n-heptane solution by a UNICAM SP 800 spectrophotometer. UV data for *N*-phenylhexamethyldisilazane (III) [7] were also used for the interpretation of the UV spectrum. Ultraviolet maxima are given in Table 3, the spectra are shown in Fig. 1.

#### Results and discussion

The bond lengths and angles for the non-hydrogen atoms are given in Table 4. An ORTEP [8] stereo diagram of the molecule is shown in Fig. 2.

The molecule (like I) has a centre of symmetry, thus the cyclodisilazane ring is planar and the two phenyl rings are parallel. All the non-hydrogen atoms ex-

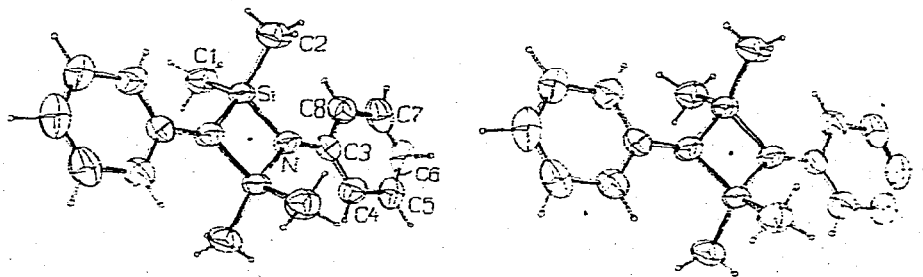


Fig. 2 An ORTEP stereo diagram of the molecule II.

\* Table of structure factors can be obtained from the authors on request.

TABLE 5

LEAST-SQUARES PLANE EQUATIONS, MEAN DEVIATIONS (Å) AND DIHEDRAL ANGLES (°).  
PLANE EQUATIONS ARE GIVEN IN THE FORM:

$AX + BY + CZ - D = 0$ , where  $X$ ,  $Y$  and  $Z$  are absolute coordinates

Plane	A	B	C	D	Mean deviation
1 Si,N,Si',N'	0.5149	0.5404	0.6654	6.0668	—
2 Phenyl group	0.5491	0.5849	0.5971	5.8577	0.003
3 Si,C(1),C(2)	0.4726	-0.8317	0.2916	3.7333	—
4 $\left\{ \begin{array}{l} \text{Si,N,Si',N'} \\ \text{C(3),C(4),C(5)} \\ \text{C(6),C(7),C(8)} \end{array} \right.$	0.5352	0.5718	0.6218	5.8990	0.037

*Dihedral angles*

1-2:	5.1				
1-3:	90.7	2-3:	93.0		
1-4:	3.3	2-4:	1.8	3-4:	92.4

cept C(1) and C(2), form a least-squares plane with 0.04 Å mean deviation. The best planes of the cyclodisilazane ring and the phenyl ring make an angle of 5.1°. The equations of the least-squares planes together with their dihedral angles are given in Table 5. The plane of Si, C(1) and C(2) atoms is nearly perpendicular to the main molecular plane (92.4°).

The Si—N bond distances 1.739(3) and 1.749(3) Å agree with other values reported (1.72(4) Å in I [1], the mean value of 1.728 Å in octamethylcyclotetrasilazane [9], 1.732(2) Å in trisilylamine [10], and 1.737(4) Å in *N*-difluoroboryldisilazane [10]). Opposing nitrogen and silicon atoms are at a distance of 2.37 and 2.56 Å, respectively, forming internal angles in the four-membered ring which deviate from 90.0°. The C—N bond length is rather short (1.382(4) Å). A slightly longer C—N bond length (1.41(1) Å) was reported [11] for dimeric phenyl isocyanate which has similar structure.

The phenyl ring is slightly distorted. The average C—C distance is 1.378 Å with two unusually short distances (C(5)—C(6) and C(7)—C(6)) opposite to the bridging (C(3)) atom. The internal bond angle at C(3) is 117.6°.

UV spectra of II and III are rather similar (cf. Table 3 and Fig. 1.). Higher absorbance values are due to the presence of two phenyl groups in compound II. Each maximum in the spectrum of II shows a considerable bathochromic shift compared to III (an increase of 23 nm in the *p*-band (258 and 235 nm) and 15–16 nm in the  $\alpha$ -band (282, 287 and 266, 272 nm)). The shoulder at

TABLE 6

PPP PARAMETERS

$i$	$I_i$ (eV)	$\gamma_{ii}$ (eV)	$i-j$	$R_{ij}$ (Å)	$\beta_{ij}$ (eV)
C	11.16	11.13	Si—N	1.739; 1.749	-1.260
N <sup>+</sup>	26.70	17.44	C—N	1.382	-2.213
Si	1.10	3.762	C—C	1.359; 1.360	-2.527
			C—C	1.384; 1.385	-2.452
			C—C	1.393	-2.415

TABLE 7  
EXPERIMENTAL AND CALCULATED ELECTRON TRANSITION ENERGIES AND OSCILLATOR STRENGTHS (eV)

Compound	$\Delta E_{\text{exp}}$ ( $f$ )	${}^1E_{\text{calc.}}$ ( $f$ )
Aniline [14]	4.40 <sup>a</sup> (0.028)	4.55 (0.054)
	5.39 <sup>a</sup> (0.144)	5.50 <sup>a</sup> (0.378)
	4.56 (0.011)	4.77 (0.027)
III [7]	4.66 (0.011)	4.80 (0.075)
	5.28 <sup>a</sup> (0.095)	5.00 <sup>a</sup> (0.554)
	4.15 (0.060)	3.78 (0.001)
II [This work]	4.32 (0.094)	4.74 (0.001)
	4.40 (0.095)	4.74 (0.036)
	4.81 <sup>a</sup> (1.079)	4.80 <sup>a</sup> (1.079)

<sup>a</sup> Denotes *p*-band.

298 nm in the spectrum of III turns into a local maximum in that of the cyclo-disilazane derivative (299 nm). Considering the coplanarity of the phenyl and cyclo-disilazane ring and the significant bathochromic shift, an enhanced conjugation can be assumed. The identically oriented *2p* electrons of the aromatic carbon atoms and the nitrogen atom form delocalized  $\pi$ -bonds with the vacant *3d* orbitals of silicon. This conjugation might possibly be greater and more stable than the 9-centre delocalized  $\pi$ -bond in III.

In order to throw light on this aspect PPP calculations were also performed [12]. The determination of the input data was carried out as described elsewhere [13]. Calculations were made for aniline, II and III, using the parameters summarized in Table 6. The calculated singlet transition energy values ( ${}^1E_{\text{calc.}}$ ) were compared with the experimental ( $\Delta E$ ) values obtained from the spectra. The results are given in Table 7. It is difficult to assign the lowest electron transitions in the experimental spectra of the two disilazane derivatives II and III, but the orders of the calculated and experimental lowest energy transitions are identical. The data for the *p*-band are well distinguished, and are in good agreement. Calculations carried out for the title compound gave the following  $\pi$ -bond orders:  $p(\text{Si}-\text{N})$  0.346 and  $p(\text{C}-\text{N})$  0.325 which agrees with the value of  $p(\text{C}-\text{N})$  0.342 calculated using Coulson's modified formula [15]. All obtained data and results of the calculations affirm the delocalized structure of compound II with  $d_{\pi}-p_{\pi}$  bonding between silicon and nitrogen.

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