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THE STRUCTURE OF TETRAMETHYL-*N*,*N'*-BIS-*o*-TOLYLCYCLODISILAZANE

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Summary

Tetramethyl-*N*,*N'*-bis-*o*-tolylcyclodisilazane was prepared in order to study the effect of *o*-substitution of the *N*-phenyl ring on the molecular structure. A crystal structure determination was carried out together with UV, ^{1}H NMR and MS spectroscopic investigations. The *o*-tolyl group forms a dihedral angle of —89.6° with the cyclodisilazane ring. This conformation is completely different from that in the two coplanar *N*-phenyl derivatives previously studied. The molecular geometry and spectroscopic data suggest decreased delocalization, in agreement with the low thermal stability. While the geometry of the cyclodisilazane moiety is unchanged, mass spectroscopic fragmentation indicates that the Si—N bonds are weaker than those in *N*-phenyl derivatives containing phenyl groups coplanar with the four-membered ring.

Introduction

The crystal structures of tetramethyl-*N*,*N'*-diphenylcyclodisilazane (I) and hexaphenylcyclodisilazane (II) of the *N*-aryl-cyclodisilazane series (Fig. 1) were described in previous papers [1,2]. The *N*-phenyl groups are almost coplanar with the planar cyclodisilazane rings in both compounds. The molecular geometries suggest delocalized bond structures. The aim of the present study is to obtain information on the changes in the molecular structure induced by the *ortho* substitution of the *N*-phenyl groups. Thus tetramethyl-*N*,*N'*-bis(*o*-tolyl)-

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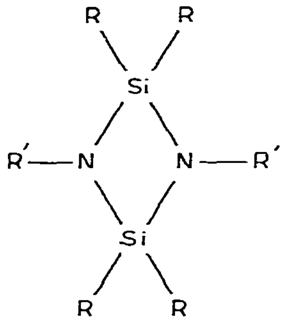

I R = CH_3, R′ = C_6H_5

II R = R′ = C_6H_5

III R = CH_3, R′ = o-$CH_3C_6H_4$

Fig. 1. The structural formula of *N*-aryl-cyclodisilazanes.

cyclodisilazane (III) was prepared and an X-ray crystal structure determination carried out along with other spectroscopic investigations.

Experimental

The disilazane III was prepared according to Fink [3]. A mixture of *o*-toluidinetriethylamine was added dropwise to a solution of dimethyldichlorosilane in benzene. The mixture was boiled for 1 h, then the triethylamine hydrochloride was filtered off and benzene was removed by distillation. Dimethylbis(*o*-toluidino)silane (b.p. 180—185°C/200 Pa) was obtained from the residue by distillation in vacuo, and was pyrolized for 6 hours while *o*-toluidine was evaporated from the system. The crude III was recrystallized from n-hexane. Yield: 81.5%. Anal. found C, 66.12; H, 8.21; N, 8.63; Si, 17.10. calcd. for $C_{18}H_{26}N_2Si_2$ C, 68.20; H, 8.02; N, 8.58; Si, 17.20%. IR absorption bands (cm^{-1}): 1488s, 1290s, 1268vs, 1250vs, 1191m, 1115s, 1045m, 970vs, 948s, 893vs, 853s, 825s, 795s, 725s.

X-ray intensity data were collected at room temperature on an Enraf-Nonius CAD4 four-circle computer-controlled single crystal diffractometer with monochromated Mo-K_α (λ = 0.71073 Å) radiation. Crystal data (from single crystal diffractometry) *a* 13.736(4), *b* 7.352(8), *c* 18.994(5) Å, *V* 1918.1(3.2) $Å^3$, D_X 1.131 mgm^{-3}, $Z = 4$, μ(Mo-K_α) 18.4 mm^{-1}, orthorhombic space group *Pbca*. A crystal of 0.35 × 0.14 × 0.14 mm was used for data collection. The surface of the crystal was coated with a layer of acrylic glue to avoid exposure to air and humidity. Three intensity check reflections were recorded hourly during data collection. The decrease of the check reflexions intensities (ca. 10% by the end of the data collection) indicated isotropic decay of the specimen. Intensity data were corrected accordingly.

The structure was determined by direct methods and refined by full-matrix least squares for 1074 observed reflexions [$I \geqslant 2.5\sigma(I)$]. Hydrogen atomic

TABLE 1

ATOMIC PARAMETERS FOR THE NON-HYDROGEN ATOMS WITH THEIR e.s.d.'s IN PARENTHESES.

B(eq.) is defined as follows: $4[(\gamma_{11}b_{22}b_{33})/(a^{*2}b^{*2}c^{*2})]^{1/3}$ (Å^2)

Atom	10^5 x/a	10^4 y/b	10^5 z/c	B(eq.)
Si	98 127 (6)	1446(1)	3327 (4)	3.81(1)
N	100 820(20)	−796(3)	5450(10)	3.55(5)
C(1)	85 820(30)	2215(5)	5610(20)	6.17(8)
C(2)	107 110(30)	3101(4)	6610(20)	5.78(8)
C(3)	104 510(20)	−1616(4)	11 680(10)	3.71(6)
C(4)	98 470(20)	−2622(4)	16 050(10)	4.30(6)
C(5)	102 690(30)	−3434(5)	22 060(10)	5.48(8)
C(6)	112 200(30)	−3256(5)	23 550(20)	6.67(9)
C(7)	118 240(30)	−2240(6)	19 330(20)	7.19(9)
C(8)	114 280(20)	−1424(5)	13 370(20)	5.41(7)
C(9)	88 050(30)	−2849(5)	14 530(20)	6.40(8)

coordinates were calculated from assumed geometries and checked in difference maps. In the last two cycles of refinement hydrogen atoms were also involved. The final R was 0.044 for the observed data. Final atomic parameters are given in Tables 1 and 2. Atomic scattering factors and anomalous dispersion coefficients were taken from ref. 4. Tables of structure factors can be obtained from the authors.

UV spectra were recorded in i-octane solution with a SPECORD UV-VIS spectrometer. UV data are shown in Table 3.

The ^{1}H NMR spectra of I, III and hexamethylcyclodisilazane (IV, R = R′ = CH_3) were obtained with a JEOL FX-100 spectrometer (at 100 MHz, in $CDCl_3$, TMS). ^{1}H NMR chemical shifts of the $SiCH_3$ groups are given in Table 4.

Mass spectra were obtained on a JEOL-OlSG-2 spectrometer using the direct insertion system. The pressure in the electron-impact ion source was 1—3 × 10^{-4}

TABLE 2

HYDROGEN ATOM PARAMETERS (X10^3) AND H—C DISTANCES WITH THEIR e.s.d.'s IN PARENTHESES

Atom	x/a	y/b	z/c	B(Å^2)	H—C (Å)
H(1A)	856(2)	248(4)	101(1)	8.3(9)	0.88(3)
H(1B)	837(2)	332(4)	33(2)	8.3(1.0)	0.97(3)
H(1C)	810(3)	156(5)	39(2)	6.7(1.1)	0.89(4)
H(2A)	1140(2)	277(5)	54(2)	7.4(9)	1.00(3)
H(2B)	1074(2)	314(5)	112(2)	9.2(1.0)	0.87(3)
H(2C)	1062(3)	432(5)	51(2)	10.0(1.1)	0.95(4)
H(5)	978(2)	−409(4)	244(1)	5.2(7)	0.93(3)
H(6)	1159(2)	−370(5)	280(2)	9.3(1.0)	1.04(3)
H(7)	1262(2)	−199(5)	199(1)	8.9(1.0)	1.12(3)
H(8)	1187(2)	−83(4)	109(1)	5.2(7)	0.89(3)
H(9A)	855(3)	−380(5)	178(2)	10.4(1.2)	1.00(4)
H(9B)	868(2)	−315(5)	98(2)	10.9(1.1)	0.94(3)
H(9C)	841(2)	−182(5)	144(2)	8.5(1.2)	0.93(4)

TABLE 3

UV DATA FOR CYCLODISILAZANES

Compound	CT bands		α band	
	λ_{max}(nm)	log ε	λ_{max}(nm)	log ε
I	205	4.57	282	3.55
	221	3.75	288	3.55
	260	4.57	301	3.36
II	197	5.05	266	3.89
	225	4.53	274	3.71
	254	4.38		
III	197	5.08	269	3.28
	210	4.80	276	3.32
	245	4.18	285	3.22
			296	3.08

Pa, the ionizing energy 75 eV, the electron emission current 200 μA and the ion-accelerating voltage 10 kV. The temperature in the ion source was 360—400 K. III gives mass spectra characteristic for *N*-phenyl-cyclodisilazanes [5]. The base peak is the molecular ion $M^{+\cdot}$ (*m/z* 326). The most characteristic fragment ion is $[M-\mathrm{Me}]^+$ (*m/z* 311), though $[\mathrm{SiMe_3}]^+$ (*m/z* 73) $[o\text{-}\mathrm{CH_3C_6H_4}\text{—N=Si(CH_3)_2}]^+$ (*m/z* 163) and $[\mathrm{C_6H_4}\text{—N=Si(CH_3)_2}]^+$ (*m/z* 148) ions are observed with significant intensity. The contribution of the doubly-charged molecular ion to the intensity of the peak at 163 is negligible since the double-charged ion (*m/z* 163.5) of the isotopic peak (*m/z* 327) is hardly observable.

Discussion

The molecule with the atomic numbering is depicted in Fig. 2, the bond distances and angles are given in Table 5. The molecular symmetry, similarly to I, is $\bar{1}$. The conformation is completely different from that in I and II. The phenyl ring of the *o*-tolyl group $[0.207X - 0.8195Y - 0.5344Z = -2.7529]$ forms a dihedral angle of —89.6° with the cyclodisilazane ring $[-0.9745X - 0.2236Y - 0.0206Z = 13.3853]$, in contrast to the coplanar structure of I and II. The elongated N—C(3) bond [1.422(3) Å vs. 1.382(4) in I and 1.388(3) Å in II, cf. Table 5] indicates reduced delocalization. A similar conclusion may be derived from the UV spectrum (Table 3) which is significantly different from the spectra of other *N*-aryl-cyclodisilazanes [6]. Owing to the decreased deloca-

TABLE 4

^{1}H NMR CHEMICAL SHIFTS OF THE $\mathrm{SiCH_3}$ GROUPS IN CYCLODISILAZANES (ppm/TMS)

Compound	$\delta(^1\mathrm{H})$	
I	0.62s	0.63s (ref. 7)
III	0.48s	
IV	0.16s	0.11s (ref. 9)

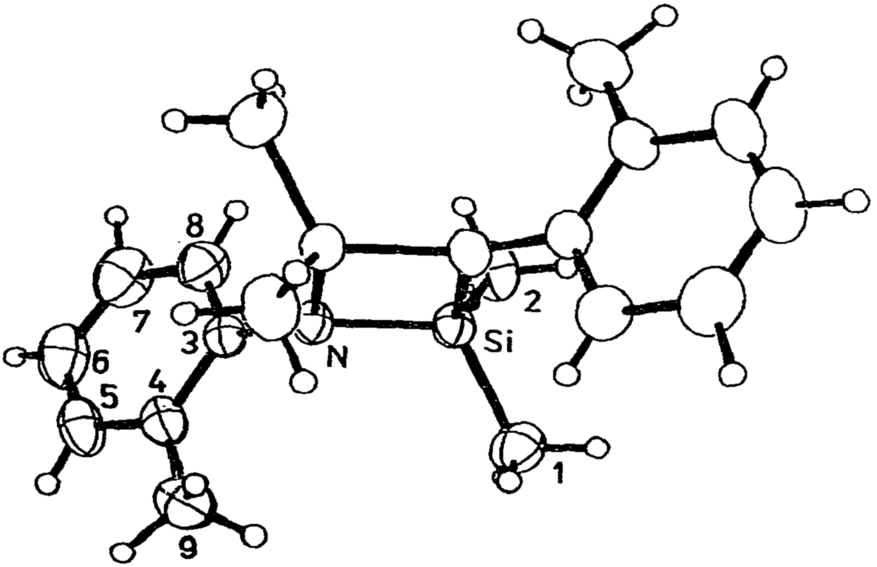

Fig. 2. The diagram of the molecule with atomic numbering. Numbers represent carbon atoms. Thermal ellipsoids are drawn at the 50% probability level.

lization, the maxima of the α- and CT-bands show hypsochromic shifts, and the intensities of the α-band maxima are lower than in I and II.

^{1}H NMR spectra are consistent with Fink's proposal [7]; i.e. the lone pairs of the nitrogen atoms in cyclodisilazanes are partially delocalized and the electron density on the nitrogen depends on the substituent. The electron density and basicity decrease in the following order:

$H > CH_3 > (CH_3)_3Si > C_6H_5$

The same order is observed in the ^{1}H NMR shifts of the $SiCH_3$ group: $\delta(^1H)$ 0.16 (CH_3), 0.24 [$Si(CH_3)_3$] [8], 0.62 ppm (C_6H_5). The decreased basicity corresponds to a higher stability towards nucleophilic attack. *o*-Tolyl substitution (III) results in reduced basicity, thus a chemical shift greater than 0.62 ppm is expected. The smaller observed value (0.48 ppm) is due to the different conformation which is most unfavourable for delocalization of the π electron system and the lone pair from nitrogen. The electron density thus becomes higher on the nitrogen atom, rendering III less stable than I and II.

In spite of the conformational difference, the mean bond length and angles in the cyclodisilazane ring [Si—N: 1.743(2) Å, N—Si—N′: 85.5(9)°, Si—N—Si′: 94.4(8)°, averaged over I, II and III] are the same within experimental error. Non-bonded Si···Si′ and N···N′ distances [Si···Si′: 2.559(2) (I), 2.591(3) (II), 2.526(1) Å (III); N···N′: 2.372(5) (I), 2.339(4) (II), 2.389(3) Å (III)] are, however, significantly different, showing that the slight differences observed in Si—N bond distances and Si—N—Si′, N—Si—N′ angles are real. The mean Si—N bond length in III [1.739(2) Å] is the shortest in the three structures studied [I: 1.744(5), II: 1.745(2) Å].

The changed conformation seems to reduce the thermal stability of III. While I (m.p. 252.5°C) and II (m.p. 355.5°C) are very stable, III (m.p. 147.0°C)

TABLE 5

BOND DISTANCES AND ANGLES WITH THEIR e.s.d.'s.

Relevant bond distances and angles are also given for I and II

Bond distances (Å)	I	II	III		
Si—N	1.739(3)	1.743(2)	1.737(2)		
Si—N'	1.749(3)	1.747(2)	1.740(2)		
Si—C(1)	1.845(4)	1.865(3)	1.834(4)		
Si—C(2)	1.852(4)	1.859(3)	1.842(4)		
N—C(3)	1.382(4)	1.388(3)	1.422(3)		
Other bonds in III					
C(3)—C(4)	1.386(4)	C(4)—C(9)	1.470(5)	C(6)—C(7)	1.375(5)
C(3)—C(8)	1.387(4)	C(5)—C(6)	1.343(6)	C(7)—C(8)	1.392(5)
C(4)—C(5)	1.413(4)				
Bond angles (°)					
	I	II	III		
Ni—Si—N'	85.7(1)	84.1(2)	86.8(2)		
N—Si—C(1)	113.9(2)	114.0(2)	115.7(2)		
N—Si—C(2)	114.7(2)	115.9(2)	113.9(2)		
N'—Si—C(1)	115.6(2)	114.8(2)	112.8(2)		
N'—Si—C(2)	114.7(2)	113.0(2)	116.7(2)		
C(1)—Si—C(2)	110.4(2)	112.3(2)	109.5(3)		
Si—N—C(3)	132.9(2)	132.6(3)	132.2(3)		
Si'—N—C(3)	132.7(2)	131.4(3)	130.7(3)		
Si—N—Si'	94.3(1)	95.8(2)	93.2(2)		
C(4)—C(3)—C(8)	117.6(3)	117.5(4)	119.7(5)		
Other angles in III					
N—C(3)—C(4)	120.7(4)	C(5)—C(4)—C(9)	120.6(5)		
N—C(3)—C(8)	119.6(4)	C(4)—C(5)—C(6)	121.9(5)		
C(3)—C(4)—C(5)	117.6(5)	C(5)—C(6)—C(7)	121.1(6)		
C(3)—C(4)—C(9)	121.8(5)	C(6)—C(7)—C(8)	118.3(6)		
		C(3)—C(8)—C(7)	121.4(5)		

decomposes when exposed to air or ionizing radiation (see above). We note that the non-bonded Si···Si' distances decrease (N···N' distances increase) as the melting points decrease.

Mass spectral data confirm the conformation effect on the stability of the cyclodisilazane ring. Thus, the characteristic $[SiMe_3]^+$ ion (m/z 73) appears with significant intensity in the mass spectrum of III but is missing from the spectra of other cyclodisilazanes [5]. This ion corresponds to cleavage of Si—N bonds, which are weaker than those in I and II. The appearance of the $[o\text{-}CH_3C_6H_4N{=}Si(CH_3)_2]^+$ ion (m/z 163) and its fragment ion $[C_6H_4N{=}Si(CH_3)_2]^+$ (m/z 148) also supports the above assumption.

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