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CONFORMATIONAL STUDY OF TETRAMETHYL-*N*,*N*′-BIS-ARYLCYCLODISILAZANES BY ^{13}C NMR AND X-RAY DIFFRACTION METHODS

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Summary

The conformations of tetramethyl-*N*,*N*′-diphenylcyclodisilazane and the corresponding bis-tolylcyclodisilazanes were studied by ^{13}C NMR spectroscopy. The conformations of tetramethyl-*N*,*N*′-bis-*m*-tolylcyclodisilazane and tetramethyl-*N*,*N*′-bis-*p*-tolylcyclodisilazane were predicted by assuming additivity of substituent chemical shifts (SCS). The conformations of the *m*- and *p*-tolyl derivatives in the crystalline state were established by crystal structure analysis, and found to be identical with those determined by ^{13}C NMR methods in solution.

Introduction

Earlier crystal structure analyses of tetramethyl-*N*,*N*′-diphenylcyclodisilazane (I) [1], tetramethyl-*N*,*N*′-bis-*o*-tolylcyclodisilazane (II) [2] and tetramethyl-*N*,*N*′-bis(3′,5′-dimethylphenyl)cyclodisilazane (V) [3] (c.f. Fig. 1) revealed the conformational features of these compounds. While *N*-aryl groups in compound I and V are fairly coplanar with the cyclodisilazane ring, *ortho*-methyl substitution (II) drastically affects this conformation and the *o*-tolyl groups adopt a position perpendicular to the cyclodisilazane ring.

The extent of conjugation between π systems strongly depends on their relative orientation, and can be readily monitored by analysis of the ^{13}C chemical shifts (see e.g. Ref. [4]). The ^{13}C NMR chemical shifts of a benzoid ring possessing more than

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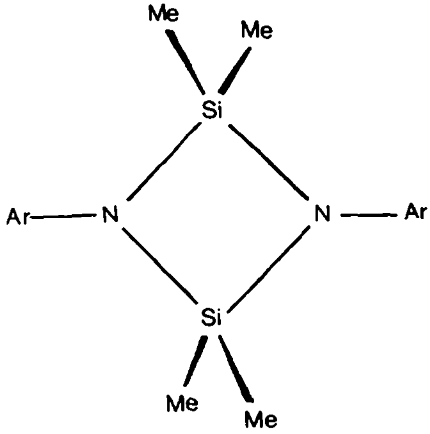
one substituent can be predicted by assuming additivity of individual substituent chemical shifts (SCS's) [5,6]. The empirical calculation of the Aromatic Chemical shifts [7] is based on chemical shift data for monosubstituted benzene derivatives,



Ar

I. C_6H_5

II. o-$CH_3C_6H_4$

III. m-$CH_3C_6H_4$

IV. p-$CH_3C_6H_4$

V. 3,5-$(CH_3)_2C_6H_3$

Fig. 1. The structural formula of tetramethyl-*N*,*N'*-diarylcyclodisilazanes.

and many data have been collected in the recent years [8]. In some cases (mainly *o*-substituted benzene derivatives), however, significant deviations are observed between measured and calculated shift values. The additivity of SCS's holds only for molecules in the same conjugation state and any interaction of the π system with other π bonds or lone electron pairs violates the additivity rule. Duddeck [9] has introduced a non-additivity parameter (NA) as a measure of these interactions:

$$NA = \delta_{\mathrm{exp}} - \delta_{\mathrm{calc}}$$

This formalism can be utilized to investigate several substituent interactions and has the advantage that it elucidates their mechanisms.

The large conformational difference between I and II offers the possibility of making a comparative study using ^{13}C NMR shifts. Two more compounds were included in further investigations tetramethyl-*N*,*N'*-bis-*m*-tolylcyclodisilazane (III) and tetramethyl-*N*,*N'*-bis-*p*-tolylcyclodisilazane (IV).

The series of the compounds I–IV comprises unsubstituted (I) and all monosubstituted derivatives (II, III, IV). X-ray crystal structure determinations were also carried out for compounds III and IV in order to reveal their conformations in the solid state.

Experimental

Synthesis

Bis-(*m*-toluidino)dimethylsilane (VI) (b.p. 186–187°C/333 Pa) and bis-(*p*-toluidino)dimethylsilane (VII) were prepared by the reaction between the appropriate toluidines and dimethyldichlorosilane in diethyl ether, as described by Anderson [10]. Triethylamine was used as HCl acceptor. The intermediates, obtained as oils, were pyrolyzed by Fink's method [11].

Compound III was obtained by a 3-h pyrolysis of VI, and was recrystallized from n-hexane and purified by sublimation. Yield: 67%. Anal. Found: C, 64.20; H, 8.25; N, 8.31; Si, 17.02. $C_{18}H_{26}N_2Si_2$ calcd.: C, 66.20; H, 8.02; N, 8.58; Si, 17.20%. M.p. 188–189°C. IR absorption bands (cm^{-1}): 1593vs, 1575vs, 1482vs, 1428m, 1328s, 1310vs, 1300vs, 1250vs, 1180vs, 1162m, 1092w, 1028s, 1011m, 992m, 969m, 908vs, 860vs, 843s, 800vs, 775s.

MS: m/z: 326 (M^+, 100%); 311 ($[M-CH_3]^+$, 74%); 163 ($M^{2+\cdot}$ and m-$CH_3C_6H_4$-N=Si$(CH_3)_2$, 13%).

Compound IV was obtained by a 2.5-h pyrolysis of VII, with recrystallization and purification as described for III. Yield: 74%. Anal. Found: C, 66.15; H, 7.37; N, 8.04; Si, 17.15. $C_{18}H_{26}N_2Si_2$ calcd.: C, 66.20; H, 8.02; N, 8.58; Si, 17.20%. M.p.

TABLE 1

CRYSTAL DATA, DATA COLLECTION AND LEAST-SQUARES PARAMETERS

	Compound III	Compound IV
Empirical formula	$C_{18}H_{26}N_2Si_2$	$C_{18}H_{26}N_2Si_2$
M(a.m.u.)	326.6	326.6
Cell constants [a] a (Å)	11.436(4)	11.732(2)
b (Å)	9.472(5)	8.230(1)
c (Å)	17.754(8)	19.849(3)
V (Å^3)	1923.1(2.6)	1916.5(8)
Space group	*Pbca*	*Pbca*
Z	4	4
Density (calc) (Mg/m^3)	1.13	1.13
Wavelength (Mo-K_α) (Å)	0.71073	0.71073
μ(Mo-K_α) (cm^{-1})	1.8	1.8
2θ-range	$3° < 2\theta < 60°$	
Scan technique	$\theta-2\theta$	
Number of reflexions collected	2792	2787
Number of reflexions with zero intensity [b]	837	865
Number of reflexions used in least-squares (NO)	1353[$I \geq 2.5\sigma(I)$]	1388[$I \geq 2.0\sigma(I)$]
Number of variables (NV)	153	153
Weighting scheme	$w = 4F_o^2/\sigma(F_o^2)^2$ $[\sigma(F_o^2) = \sigma(I)^2 + (0.01I)^2]^{1/2}/Lp]$	
R_o	0.047	0.042
R_{w_o}	0.055	0.050
R_{tot}	0.075(1955)	0.068(1922)
$(\Sigma w(\|F_o\|-\|F_c\|)^2/(NO-NV))^{1/2}$	2.5	2.6

[a] Obtained from the setting angles of 25 carefully centered reflexions. [b] Excluded from the final data set.

TABLE 2

FINAL ATOMIC COORDINATES ($\times 10^4$) AND MEAN TEMPERATURE FACTORS (Å^2)[a] FOR THE NON-HYDROGEN ATOMS WITH THEIR E.S.D.'S

Atom	Compound III				Compound IV			
	x/a	y/b	z/c	B_{eq}	x/a	y/b	z/c	B_{eq}
Si	821.2(6)	782.2(7)	252.7(4)	4.51(3)	−756.6(5)	1091.8(7)	95.7(4)	5.16(4)
N	−180(2)	821(2)	−483(1)	4.75(9)	304(1)	689(2)	−491(1)	5.4(1)
C(1)	2359(2)	668(3)	−44(2)	6.9(2)	−538(2)	2962(3)	589(1)	6.7(2)
C(2)	641(3)	2196(3)	954(2)	6.9(2)	−2225(2)	1040(3)	−234(1)	6.4(2)
C(3)	−396(2)	1820(2)	−1044(1)	4.5(1)	629(2)	1444(2)	−1089(1)	5.1(2)
C(4)	−1200(2)	1576(3)	−1610(1)	5.1(1)	1568(2)	929(3)	−1451(1)	6.2(2)
C(5)	−1428(2)	2565(3)	−2172(1)	5.7(1)	1868(2)	1641(3)	−2049(1)	6.9(2)
C(6)	−825(2)	3812(3)	−2162(2)	6.5(1)	1254(2)	2887(3)	−2326(1)	6.6(2)
C(7)	−27(2)	4091(3)	−1610(2)	6.6(1)	341(2)	3440(3)	−1960(1)	7.1(2)
C(8)	194(2)	3101(3)	−1048(1)	5.3(1)	29(2)	2751(3)	−1354(1)	6.5(2)
C(9)	−2306(3)	2263(4)	−2772(2)	8.3(2)	1562(2)	3600(4)	−3005(1)	9.2(3)

[a] Mean temperature factors are defined as $B_{eq} = 4/3\text{trace}(B \times G)$ where B is the thermal motion tensor and G is the metric tensor.

203°C. (M.p. 196–197°C [12]). IR absorption bands (cm^{-1}): 1609s, 1510vs, 1290vs, 1250vs, 1178m, 1120m, 1110m, 960vs, 900vs, 818vs, 810vs, 790s, (1613, 1515, 1282, 1250, 961, 900, 819, 813, 787 [12]).

MS: m/z: 326 (M^+, 100%); 311 (M-CH$_3]^+$, 69%); 163 ($M^{2+\cdot}$ and p-$CH_3C_6H_4$-N=Si$(CH_3)_2$, 15%).

^{13}C *NMR measurements*

^{13}C NMR spectra were recorded on a JEOL FX-100 instrument at 25.00 MHz.

TABLE 3

FINAL ATOMIC COORDINATES ($\times 10^3$), ISOTROPIC TEMPERATURE FACTORS (Å^2) AND C–H DISTANCES ($\times 10^2$ Å)

Atom	Compound III					Compound IV				
	x/a	y/b	z/c	B	C–H	x/a	y/b	z/c	B	C–H
H(1a)	284(2)	59(3)	35(1)	9.2(8)	89(2)	−107(2)	309(3)	90(1)	9.6(6)	88(2)
H(1b)	252(2)	−7(3)	−36(1)	9.4(8)	92(3)	−59(2)	387(3)	30(1)	9.2(6)	94(2)
H(1c)	260(3)	144(3)	−34(1)	10.2(8)	94(3)	15(2)	298(3)	81(1)	9.3(6)	92(2)
H(2a)	112(3)	206(3)	135(1)	10.7(9)	90(3)	−272(2)	123(3)	12(1)	8.5(6)	93(2)
H(2b)	75(2)	310(3)	76(1)	9.7(8)	93(3)	−240(2)	11(2)	−40(1)	8.7(6)	86(2)
H(2c)	−7(2)	212(3)	120(1)	10.8(8)	93(3)	−234(2)	183(2)	−55(1)	8.3(5)	91(2)
H(4)	−162(2)	71(2)	−161(1)	5.0(6)	95(3)	200(2)	5(2)	−127(1)	6.8(5)	95(2)
H(5)						250(2)	127(3)	−229(1)	8.5(6)	93(2)
H(6)	−92(2)	444(3)	−255(2)	8.3(8)	92(3)					
H(7)	41(2)	497(3)	−162(1)	7.3(7)	97(3)	−10(2)	428(3)	−211(1)	8.3(6)	91(2)
H(8)	74(2)	330(3)	−65(1)	6.8(6)	96(2)	−61(2)	316(2)	−109(1)	6.8(5)	98(2)
H(9a)	−234(3)	294(3)	−312(2)	11.9(9)	89(3)	108(2)	441(3)	−310(1)	11.9(8)	89(2)
H(9b)	−214(3)	143(3)	−306(2)	12.3(9)	96(3)	152(2)	279(3)	−334(1)	12.3(8)	94(2)
H(9c)	−305(3)	208(3)	−257(2)	10.7(8)	94(3)	230(2)	403(3)	−299(1)	11.8(8)	94(2)

Samples were taken in $CDCl_3$ solution and TMS was used as internal standard. The standard spectral conditions were as follows: flip angle: 30°, spectral width: 5000 Hz, pulse delay: 2 s, data points: 16 K.

The spectrum of II was also recorded at 75.46 MHz using a Bruker WH-300 instrument.

X-ray structure determinations

The determination of unit cell dimensions and intensity data collections were performed on a computer controlled Enraf-Nonius CAD-4 diffractometer at room temperature (19°C). Crystal data, data collection and least-squares parameters are shown in Table 1.

Both structures were solved by direct methods (MULTAN-78, [13]) and were refined by full-matrix least-squares for the non-hydrogen atoms. Hydrogen atom coordinates were generated from assumed geometries and were checked in difference maps. In two final cycles the hydrogen atoms (positional parameters and isotropic temperature factors) were also included in the refinement. Atomic scattering factors were taken from Ref. [14], and no absorption correction was applied. Final atomic parameters are given in Tables 2 and 3. Lists of structure factors and anisotropic temperature factors may be obtained from the authors.

Results

The ^{13}C chemical shifts are listed in Table 4. The assignment for II was supported by selective $^{13}C\{^1H\}$ decoupling. The substituent chemical shifts for the tetramethylcyclodisilazane moiety were derived from the data for I. The chemical shifts for compounds II–IV were calculated using the above reference (I) and data from Ref. [8]. The non-additivity effects (*NA*) were then calculated and are shown in Table 5. The *NA* effects for III and IV are in the range of $-0.1 - +0.4$ ppm, and significant deviations are observed for II. These findings indicate that aromatic rings in compound I, III and IV are in the same conjugation state, and this is also confirmed by crystal structure determinations, i.e. the three rings in these compounds are nearly coplanar in the dominant conformation.

ortho-Methyl substitution in II would result in unfavourably close contacts between *o*-methyl groups and the cyclodisilazane moiety in the coplanar conforma-

TABLE 4

^{13}C NMR CHEMICAL SHIFTS FOR COMPOUNDS I–IV (δ_{TMS} 0.0 ppm). Atomic numbering refers to that used in the crystallographic study (c.f. Figs. 2 and 3)

	I	II	III	IV
C(3)	146.3	143.7	146.2	143.6
C(4)	117.9	131.8	118.4	117.6
C(5)	129.6	130.9	139.3	130.1
C(6)	118.4	124.9	119.1	127.4
C(7)	129.6	126.5	129.4	130.1
C(8)	117.9	121.5	114.8	117.6
$Si(CH_3)_2$	1.5	3.8	1.5	1.5

TABLE 5

NON-ADDITIVITY PARAMETERS (*NA*) FOR COMPOUNDS II–IV (for the numbering of atoms see Figs. 2 and 3)

	II	III	IV
C(3)	−3.2	0.1	0.4
C(4)	−4.6	0.1	0.3
C(5)	−0.7	0.4	0.1
C(6)	−6.5	−0.1	0.3
C(7)	0.0	0.2	0.1
C(8)	−3.6	0.0	0.3

tion. The planes of the aryl groups are perpendicular to the plane of the cyclodisilazane ring and the rotation about the N–C(3) bond is hindered. The *NA* effects show that interaction between *o*-methyl group and cyclodisilazane ring affects not only

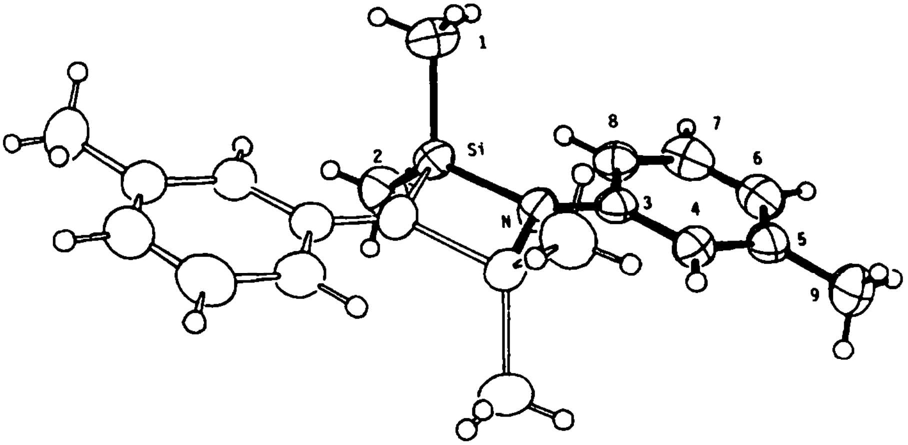


Fig. 2. Molecular diagram of III. Numbers are for carbon atoms unless indicated otherwise.

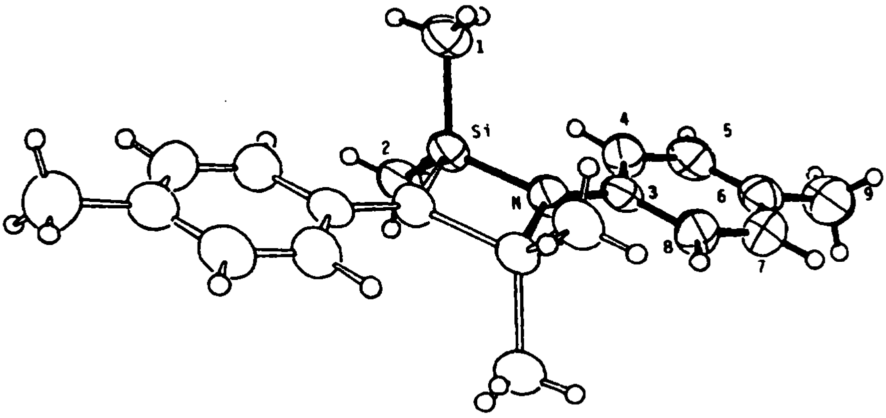


Fig. 3. Molecular diagram of IV. Numbers are for carbon atoms unless indicated otherwise.

TABLE 6

RELEVANT BOND DISTANCES AND ANGLES

	Compound III	Compound IV
Bond distances (Å)		
Si–N	1.737(2)	1.736(2)
Si–N′	1.735(2)	1.745(2)
Si–C(1)	1.839(3)	1.842(3)
Si–C(2)	1.840(3)	1.843(3)
N–C(3)	1.396(3)	1.393(3)
Bond angles (°)		
N–Si–C(1)	114.6(2)	114.6(2)
N–Si–C(2)	114.8(2)	115.3(2)
N–Si–N′	85.2(2)	85.6(1)
C(1)–Si–C(2)	110.1(2)	109.8(2)
C(1)–Si–N′	114.8(2)	114.9(2)
C(2)–Si–N′	115.5(2)	115.1(2)
Si–N–C(3)	131.9(3)	133.0(2)
Si–N–Si′	94.8(2)	94.4(1)
C(3)–N–Si′	133.4(3)	132.4(2)
Non-bonded distances (Å) in the cyclodisilazane ring		
Si ··· Si′	2.555(1)	2.555(1)
N ··· N′	2.352(3)	2.365(3)

δ(C(3)) and δ(C(4)) (the numbering of atoms refers to that used in the crystallographic study, c.f. Figs. 2 and 3), but also δ(C(6)), while δ(C(5)) and δ(C(7)) are not influenced considerably. These results indicate that *o*-methyl substitution causes significant change in the π-system showing that different conformation is not caused exclusively by avoiding non-bonded interactions. Significant differences between I, III, IV and II have been observed also in Si-methyl ^{13}C chemical shifts.

The conformations of III and IV in the crystalline state (Figs. 2 and 3) correspond to those expected from the NMR study. It is likely that dominant conformations in solution are indentical with those found in crystal structures.

Both molecules possess inversion center. The best planes of the phenyl rings (III: $0.71897X - 0.40543Y - 0.56454Z = 0.02075$; IV: $-0.58575X - 0.64637Y - 0.48898Z = -0.15685$) and the cyclodisilazane rings (III: $0.65522X - 0.47464Y - 0.58772Z = 0$; IV: $-0.65107X - 0.52787Y - 0.54540Z = 0$) form dihedral angles of 5.6° (III) and 8.4° (IV), respectively. Relevant bond distances and angles (Table 6) agree with data obtained for compound I [1].

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