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

II *. THE CONFORMATION OF TETRAMETHYL-*N*,*N*′-BIS(*o*-CHLOROPHENYL)CYCLODISILAZANE

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Summary

NMR data indicate that tetramethyl-*N*,*N*′-bis-*o*-chlorophenylcyclodisilazane possesses aryl groups which are coplanar with the cyclodisilazane ring. An X-ray crystal structure determination has corroborated this conformation in the solid state. The Si–N bond distance (1.756(2) Å) is the longest reported for *N*,*N*′-diarylcyclodisilazanes. Interaction between the halogen atom and *d*–orbitals of silicon and enhanced delocalization may contribute to the stability of the coplanar conformation. Repulsive non-bonded interactions in the coplanar conformation are presumably less prominent than in the *o*-tolyl derivative.

Introduction

The results of conformational studies on tetramethyl-*N*,*N*′-bis-arylcyclodisilazanes (Fig. 1, compounds I, II, III and IV) using ^{13}C-NMR and X-ray diffraction methods were reviewed in the previous paper [1].

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* For Part I see Ref. [1].

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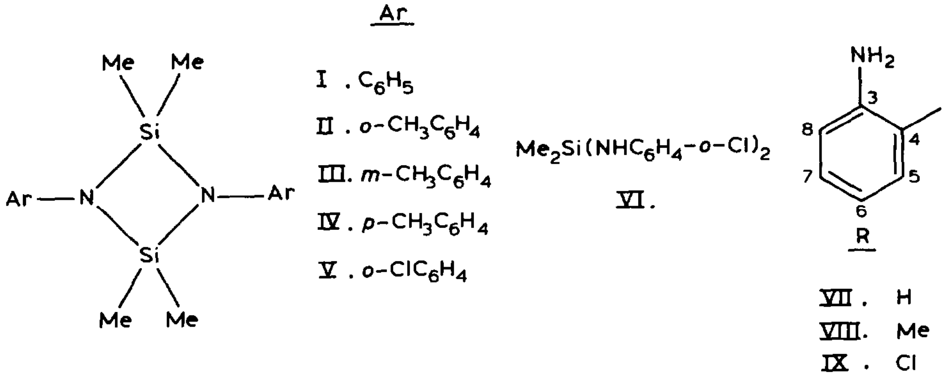

Fig. 1. Chemical formulae for compounds I–IX.

Two types of conformation were established by X-ray diffraction:

a) "coplanar" (compounds I, III and IV), i.e. the aryl groups are coplanar with the cyclodisilazane ring;

b) "perpendicular" (compound II), i.e. the aryl groups are perpendicular to the cyclodisilazane ring.

These conformations were related to ^{13}C-NMR data using the additivity of the substituent chemical shifts (SCS's) for the aromatic ring atoms. The non-additivity parameters (NA) were obtained using the ^{13}C-NMR chemical shifts of I and data from the literature. Significant NA-parameters were found for II, showing that the aryl ring is in a conjugation state markedly different from that in I, III and IV. The NA parameters for II also show that the perpendicular conformation may not be exclusively attributable to the steric effects of the substituent in the *o*-position but also to the significant changes in the π-system.

Application of the additivity of the SCS's to the title compound (V) predicts the existence of the less expected coplanar conformation. This finding showed the need of an X-ray structure determination and further investigations.

Experimental

Synthesis

Bis(*o*-chloroanilino)dimethylsilane (VI, b.p. 171-172°C/53 Pa) was prepared by the reaction of *o*-chloroaniline with dimethyldichlorosilane in diethyl ether solution, according to the method of Anderson [2]. VI was pyrolized by Fink's method [3] for 4 h at 330–340°C. The product was recrystallized from acetone and purified by sublimation to give V: (41%), m.p. 221–222°C. (Found: C, 52.22; H, 5.40; N, 7.71; Si, 14.92. $C_{16}H_{20}Cl_2N_2Si_2$ calcd.: C, 52.30; H, 5.49; N, 7.62; Si, 15.29%); IR (cm^{-1}) 342 w, 400 w, 438 w, 750 s, 800 s, 885 s, 955 vs, 1041 vs, 1055 s, 1130 m, 1158 m, 1260 s, 1270 s, 1312 s, 1432 s, 1475 vs, 1580 s; MS *m/e*: 366 (90%) (M^+), 351 (100%) $(M\text{-}CH_3)^+$, 93 (38%) $(CH_3)_2Si^+Cl$, [^{35}Cl].

NMR measurements

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL FX-100 instrument (2.3 T) with a tunable probe. Samples were taken in $CDCl_3$ solution and TMS was used

TABLE 1

CRYSTAL DATA, DATA COLLECTION AND LEAST-SQUARES PARAMETERS

Empirical formula	$C_{16}H_{20}N_2Cl_2Si_2$
M(a.m.u.)	367.4
a(Å)	23.708(2)
c(Å)	8.557(1)
V(Å^3)	4165.3(1.2)
Space group	$R\bar{3}$
Z	3
D_c (g cm^{-3})	1.318
λ (Mo-K_α) (Å)	0.71073
μ(Mo-K_α) (cm^{-1})	4.8
2θ limits, deg	3–60
Scan technique	θ–2θ
Reflexions with non-zero intensity	1878
Reflexions used in least squares, NO	1378 [$I \geqslant 2.5\sigma(I)$]
Number of variables, NV	100
Weighting scheme [a]	$w = 4I\mathrm{L}/(\sigma(I)^2 + (0.01I^2)$
R_o	0.058
R_w	0.070
R_{tot}	0.090
$(\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\mathrm{NO}-\mathrm{NV}))^{1/2}$	2.9

[a] Where I is the intensity and L is the Lorentz-polarization factor.

TABLE 2

FINAL ATOMIC COORDINATES ($\times 10^4$) AND B(eq) [a] VALUES (Å^2) FOR THE NON-HYDROGEN ATOMS

Atom	x/a	y/b	z/c	B(eq)
Cl	6387.2(6)	646.4(7)	8029(2)	7.74(4)
Si	4854.3(4)	288.7(4)	3923(1)	2.81(2)
N	5451(1)	508(1)	5377(3)	3.02(7)
C(1)	5222(2)	453(2)	1953(4)	4.08(9)
C(2)	4342(2)	658(2)	4265(5)	4.0(1)
C(3)	5944(2)	1126(2)	5785(4)	3.24(9)
C(4)	6400(2)	1268(2)	6971(4)	4.1(1)
C(5)	6876(2)	1911(2)	7348(5)	5.4(1)
C(6)	6909(2)	2408(2)	6499(7)	6.7(2)
C(7)	6488(2)	2285(2)	5326(7)	5.9(1)
C(8)	6022(2)	1675(2)	4938(6)	5.2(1)

[a] B(eq) is defined as 4/3trace(B G) where B is the thermal motion tensor, G is the real metric tensor.

as internal standard. ^{13}C multiplicities were verified by APT (attached proton test). ^{1}H NMR (ppm) 0.73 ($SiCH_3$, s, 12H), 6.5–6.7 (ArH, m, 4H), 6.9–7.3 (m, 4H). ^{13}C NMR (ppm) 4.8 $SiCH_3$, 143.6 C(3) *, 122.3 C(4), 130.3 C(5), 120.3 C(6), 127.4 C(7), 119.0 C(8) ^{29}Si NMR (ppm) 6.23.

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* For the numbering of atoms see Fig. 2.

TABLE 3

CALCULATED ATOMIC COORDINATES ($\times 10^3$) FOR THE HYDROGEN ATOMS [a,b]

Atom	x/a	y/b	z/c
H(1a)	489	33	119
H(1b)	553	90	185
H(1c)	544	21	180
H(2a)	403	53	346
H(2b)	413	52	525
H(2c)	461	112	427
H(5)	717	199	819
H(6)	723	284	673
H(7)	652	264	475
H(8)	574	161	408

[a] C–H = 0.95 Å. [b] Isotropic B values of the hydrogen atoms are derived from the B(eq) values of the carbon atoms to which they are bonded using the relation $B(\mathrm{H}) = B(\mathrm{eq}) + 1.0$ (Å^2).

X-ray structure determination

The determination of the unit cell dimensions and the collection of intensity data 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 given in Table 1.

The structure was solved by the MULTAN program [4] and was refined by full-matrix least-squares for the non-hydrogen atoms. Positional parameters for the hydrogen atoms were generated from assumed geometries and checked in difference maps. Published atomic scattering factors [5] were used, and no absorption correction was applied. The final atomic parameters are listed in Tables 2 and 3. Lists of observed and calculated structure factors and anisotropic temperature parameters may be obtained from the authors.

Discussion

NMR results

The coplanar conformation of V has been established using ^{1}H and ^{13}C-NMR spectroscopy. A comparison of the ^{1}H NMR chemical shifts for the $SiCH_3$ signal of I and V shows that the *o*-chloro substitution causes a 0.11 ppm downfield shift. This is in agreement with the decreased basicity of the nitrogen atom [6]. No anomalous upfield shift has been observed to overcompensate this, as was noticed for the perpendicular conformation [7].

In the preceding paper [1] we showed that the aromatic ^{13}C chemical shift additivity parameters differed slightly for the coplanar and the perpendicular conformations. Using the ^{13}C chemical shifts for I, the chemical shifts of the substituted derivatives having a coplanar conformation can be predicted with only small errors. Significant non-additivity ($\mathrm{NA} = \delta_{\mathrm{exp}} - \delta_{\mathrm{calc}}$) [8] was noticed for II (perpendicular conformation) indicating a different conjugation state. Non-additivity parameters have been calculated for V in the same manner (Table 4). Some NA values, however, were considerably higher (NA > 1 ppm for C(3) and C(4)) so that the conformation could not be established in this way. The mean of the absolute

TABLE 4

NON-ADDITIVITY PARAMETERS (NA) (ppm) FOR COMPOUNDS II, V, VIII AND IX

Compound	C(3) [a]	C(4)	C(5)	C(6)	C(7)	C(8)	Mean value [b]
II	−3.2	−4.6	−0.7	−6.5	0.0	−3.6	3.10
V	−3.1	−1.9	0.3	0.5	−0.4	−0.3	1.08
VIII [c]	0.4	−1.5	0.5	2.1	0.8	−0.2	0.92
IX	−6.1	−1.6	−0.2	1.2	0.4	0.1	1.60

[a] For the numbering of atoms see Fig. 2. [b] $\sum_{i=3}^{8} |NA(C_i)|/6$. [c] For the numbering of atoms see Fig. 1.

values of the NA parameters does not give the correct information, either. The NA parameters of V and II were therefore compared to those of simple aromatic model compounds (VIII and IX in Table 4). Literature data was used for chemical shift [9] and substituent-induced shifts [10]. The mean values of the NA parameters are in good agreement for the chloro-substituted compounds, while they differ considerably for the methyl-substituted ones. The conjugation of the π-system and the nitrogen lone-pair may be monitored by the chemical shifts of C(4), C(6) and C(8) atoms, (C(6) being free from steric effects (see Fig. 2). Thus, the NA-effect for C(6) can be indicative of the conformation. Contrary to the situation for II, no characteristic difference is observed between the experimental and calculated C(6) chemical shifts for V, so a coplanar arrangement can be inferred. The NA-effects for C(3) and C(4) in V and IX show that some additional interactions may exist between the halogen and nitrogen. This is more as usual for IX than for V since the nitrogen atoms in the latter are influenced by silicon *d*–orbitals.

The description of the crystal structure

The molecular diagram with the numbering of atoms is given in Fig. 2. The molecule has coplanar conformation, as indicated by the NMR study. The dihedral

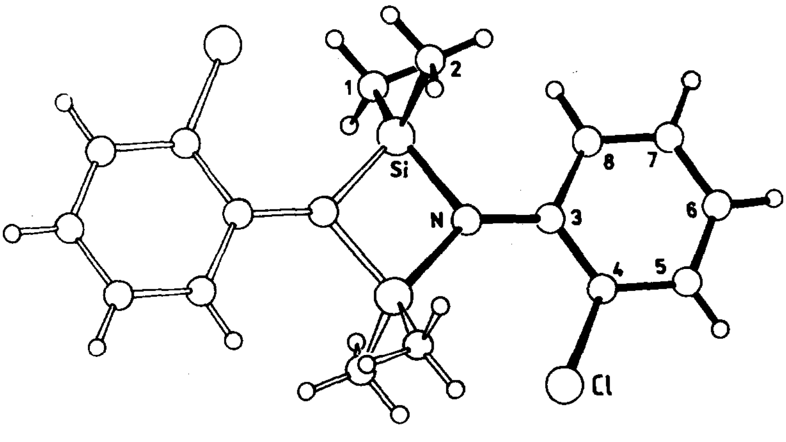

Fig. 2. Diagram of the molecule (V) with numbering of the carbon atoms.

TABLE 5

BOND LENGTHS AND ANGLES WITH ESTIMATED STANDARD DEVIATION IN PARENTHESES

Bond lengths (Å)					
Cl–C(4)	1.717(3)	Si–C(2)	1.841(3)	C(4)–C(5)	1.408(5)
Si–N	1.756(2)	N–C(3)	1.386(4)	C(5)–C(6)	1.353(5)
Si–N′	1.756(2)	C(3)–C(4)	1.396(5)	C(6)–C(7)	1.341(7)
Si–C(1)	1.848(4)	C(3)–C(8)	1.419(4)	C(7)–C(8)	1.351(5)

Bond angles (°)					
N–Si–C(1)	111.0(2)	Si–N–Si′	94.9(2)	Cl–C(4)–C(5)	118.0(5)
N–Si–C(2)	111.8(2)	C(3)–N–Si′	136.6(3)	C(3)–C(4)–C(5)	122.2(5)
N–Si–N′	85.1(2)	N–C(3)–C(4)	125.5(5)	C(4)–C(5)–C(6)	119.1(6)
C(1)–Si–C(2)	113.5(3)	N–C(3)–C(8)	119.7(5)	C(5)–C(6)–C(7)	120.0(7)
C(1)–Si–N′	115.8(2)	C(4)–C(3)–C(8)	114.8(5)	C(6)–C(7)–C(8)	122.6(7)
C(2)–Si–N′	116.2(2)	Cl–C(4)–C(3)	119.8(5)	C(3)–C(8)–C(7)	121.2(6)
Si–N–C(3)	128.3(3)				

Non-bonded distances (Å) in the cyclodisilazane ring	
Si...Si′	2.587(1)
N...N′	2.375(3)

angle between the plane of the cyclodisilazane ring and the weighted best plane of the phenyl ring is 3.8(1)°.

The molecule has a center of inversion similar to I, II, III and IV. The N–C(3) bond distance (1.386(4) Å) indicates partial double-bond character (bond lengths and angles are listed in Table 5). The lengths of both Si–N bonds are equal (1.756(2) Å) and the longest reported for N,N'-diarylcyclodisilazanes. Relevant data on the molecular geometries of N,N'-diarylcyclodisilazanes are shown in Table 6.

Slight distortions in the molecular geometry decrease repulsive non-bonded interactions. The chlorine atom is out of the plane of the phenyl ring by 0.068(2) Å and the N–C(3)–C(4) bond angle is larger by 5.8° than the N–C(3)–C(8) angle. The greatest distortion is observed in the C(3)–N–Si′ bond angle (136.6(3)°) compared to C(3)–N–Si (128.3(3)°).

The length of Si–C(Me) bonds obtained from X-ray crystal structure determinations are generally too short (a mean of 1.844 Å is observed in the title compound). Use of a riding motion correction [14] results in a bond distance of 1.861 Å for both Si–C bonds.

Factors stabilizing the coplanar conformation

Intramolecular interactions between the *d*-orbitals of silicon and halogen atoms in α-positions are frequently assumed (e.g. [15]) though geometric data are rarely reported. A 3.09 Å long Si...Cl interaction was found in 1-chloromethyl-3,7-dimethylsilatrane [16]. The Cl...Si′ $[1-x,-y,1-z]$ intramolecular close contact (3.137 Å) in V falls in the same range. This value is shorter by 0.76 Å than the sum of the van der Waals radii (3.90 Å [17]). A geometrically favourable five-membered ring is

TABLE 6

RELEVANT GEOMETRIC DATA FOR *N,N'*-DIARYLCYCLODISILAZANES[a]

Compound	Ar	R	Si–N	Si...Si	N...N	N–Si–N	Si–N–Si	N–Ar	dihedral angle[b]	Ref.
I	C_6H_5	CH_3	1.739(3) 1.749(3)	2.559(2)	2.372(5)	85.7(1)	94.3(1)	1.382(4)	5.1	11
II	*o*-$CH_3C_6H_4$	CH_3	1.737(2) 1.740(2)	2.526(1)	2.389(3)	86.8(2)	93.2(2)	1.422(3)	89.6	7
III	*m*-$CH_3C_6H_4$	CH_3	1.735(2) 1.737(2)	2.555(1)	2.352(3)	85.2(2)	94.8(2)	1.396(3)	5.6(1)	1
IV	*p*-$CH_3C_6H_4$	CH_3	1.736(2) 1.745(2)	2.555(1)	2.365(3)	85.6(1)	94.4(1)	1.393(3)	8.4(1)	1
V	*o*-ClC_6H_4	CH_3	1.756(2) 1.756(2)	2.587(1)	2.375(3)	85.1(2)	94.9(2)	1.386(4)	3.8(1)	this work
	C_6H_5	C_6H_5	1.743(2) 1.747(2)	2.591(3)	2.339(4)	84.1(2)	95.8(2)	1.388(3)	3.5	12
	3,5-$(CH_3)_2C_6H_3$	CH_3	1.736(2) 1.737(2)	2.559	2.349	85.1(1)	94.9(1)	1.412(4)	2.1	13
	2,4,6-$(CH_3)_3C_6H_2$	$(CH_3)_3C$;F	1.732(4) 1.726(4)	2.506	2.383	87.1(2)	92.9(2)	1.447(5)	67.1	13

[a] Distances are given in Å and angles in degrees. [b] Formed by the plane of the cyclodisilazane ring and the phenyl ring.

formed (with a 85.6° angle at the chlorine atom) thus the existence of such a Si...Cl interaction cannot be ruled out.

A chlorine-bridged structure is further substantiated by the low resolution MS spectrum, where a $[(CH_3)_2SiCl]^+$ fragment (*m/e* 93) is detected with a significant intensity (38%). The overall molecular geometry seems to favour the production of this ion. It is noteworthy though that no significant difference is observed in the ^{29}Si NMR chemical shifts of II and V (the ^{29}Si chemical shifts for the discussed compounds are as follows: I 5.98, II 6.18, III 6.34, IV 5.94, V 6.23 ppm).

CNDO/2 calculations were performed for VII, VIII and IX in order to reveal the electronic effect of the substituents on the carbon atom which is linked to nitrogen. The calculated partial charges on C(N) are as follows: VII +0.1541, VIII +0.1396 and IX +0.1671. Assuming that an interaction with the lone pair from nitrogen is more readily achieved through a positively charged carbon atom, it seems to be apparent that *o*-chloro substitution activates such an interaction. An *o*-methyl substituent, on the other hand, results in the least positively charged C(N). Enhanced delocalization in the title compound may contribute to the stabilization of the coplanar conformation. The relatively long Si–N bonds may also be accounted for by the more extensive delocalization with the aryl π-system.

Repulsive non-bonded interactions in the coplanar conformation are probably not so important in V as in II. Van der Waals interactions between atoms of the aryl group and the rest of the molecule were calculated for both compounds as a function of the rotation about the N–C(3) bond. The function is plotted in Fig. 3. The form of the potential function used was:

$$E = -Ar_{ij}^{-6} + Br_{ij}^{-n} \exp(-\alpha r_{ij})$$

where r_{ij} is the interatomic distance between atoms *i* and *j*. The potential coefficients (*A*, *B*, *n* and α) were taken from ref. [18]. Since no reliable coefficients for silicon interactions are available, the coefficients given for sulphur (identical to those used for chlorine) were applied to silicon. The plot was drawn so that the minimum energy values obtained for each curve were taken as equal and arbitrarily assigned as

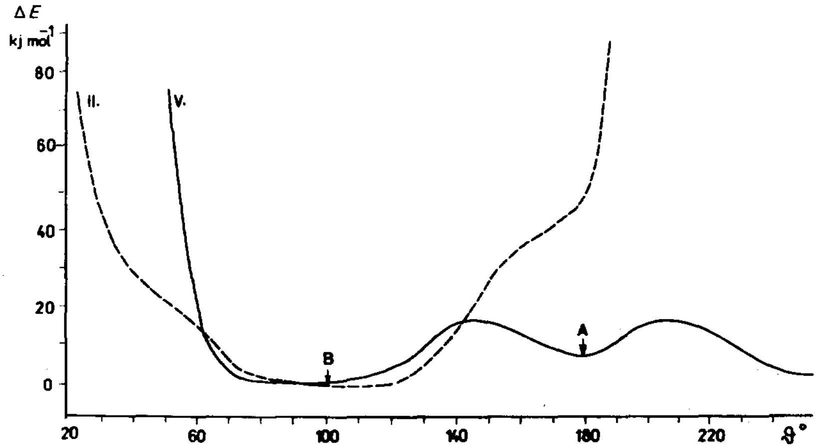

Fig. 3. The potential function plotted against the torsion angle ϑ (C(4)–C(3)–N–Si) for compounds II and V.

zero. Though numerical values in these calculations may not be taken literally, due to the incompletely justifiable choice of the potential coefficients for silicon, the distortions in the molecular geometry and the neglect of the rotations of the methyl groups, they still offer a comparison of the Van der Waals interactions.

Both II and V in the perpendicular conformation are in minimum energy state with respect to Van der Waals interactions. Rotating the *o*-tolyl group of II the energy steadily rises. The energy value equivalent to the observed torsion angle for V (point A in Fig. 3) is slightly higher than zero but repulsive interactions are still negligible. The asymmetry of the potential curve is due to the distortions in the molecular geometry.

The differences in the Van der Waals radii for the methyl group and chlorine (2.00 and 1.80 Å [17]) and in the $C(sp^2)$–Cl and $C(sp^2)$–$C(sp^3)$ bond distances establish more favourable conditions for the coplanar conformation for V than for II. Other stabilizing factors already mentioned may compensate for the steric effects.

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