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CONFORMATIONAL STUDY OF TETRAMETHYL-*N*,*N'*-BIS-ARYL-CYCLODISILAZANES BY ^{13}C NMR AND X-RAY DIFFRACTION ANALYSIS

III *. THE CONFORMATION OF TETRAMETHYL-*N*,*N'*-BIS(*O*-METHOXYPHENYL)CYCLODISILAZANE

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Summary

The conformation of tetramethyl-*N*,*N'*-bis(*o*-methoxyphenyl)cyclodisilazane was investigated by ^{13}C NMR in solution and by X-ray diffraction in the solid state. The conformation in solution compares to that of *o*-methoxyaniline. The phenyl and the cyclodisilazane ring forms a dihedral angle of 7.4° and there is a non-bonded Si · · · O distance of 2.73 Å in the crystal. The molecular geometry suggests an analogy to S · · · O non-bonded interactions often observed in organosulphur chemistry.

Introduction

In the course of a systematic study on the conformation of *N*,*N'*-bis-aryl-cyclodisilazanes seven compounds have been synthesized and their crystal structures analysed. The compounds I–IV comprise unsubstituted I and all mono-Me substituted (II–IV) *N*-phenyl derivatives. V and VI are *N*-*o*-phenyl substituted molecules. The conformational effect of the bulky phenyl rings linked to silicon was investigated using the perphenylated compound VII. Crystals of compounds I–VII

* For Part II see ref. 4.

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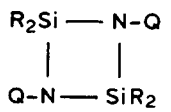

	R	Q	Molecular symmetry	Ref.
I	CH_3	C_6H_5	$\bar{1}$	1
II	CH_3	*o*-$CH_3C_6H_4$	$\bar{1}$	2
III	CH_3	*m*-$CH_3C_6H_4$	$\bar{1}$	3
IV	CH_3	*p*-$CH_3C_6H_4$	$\bar{1}$	3
V	CH_3	*o*-ClC_6H_4	$\bar{1}$	4
VI	CH_3	*o*-$CH_3OC_6H_4$	$\bar{1}$	this work
VII	C_6H_5	C_6H_5	2	5

possess molecular crystallographic symmetry operators which, for comopunds I–VI is the inversion centre ($\bar{1}$), and for VII, the two-fold axis (2). The presence of an inversion centre in these molecules requires strictly planar four-membered rings while the two-fold axis permits ring puckering. Puckering of the cyclodisilazane ring in VII, however, is slight: the two half-rings are folded along one of the diagonals forming a dihedral angle of 1.2°. Thus ring planarity of cyclodisilazane moieties seems to be a characteristic conformational feature. This is further supported by a recent electron diffraction study (R = Q = Me, [6] and other crystal structure determinations (e.g. [7]).

Compound I was the first simple symmetric *N*-aryl-cyclodisilazane studied by X-ray diffraction. The phenyl rings are fairly coplanar, with the cyclodisilazane moiety establishing a favourable orientation of the aryl π-electron system allowing interaction with the $2p$ lone electron pair of the nitrogen atom. The N–C bond distance appears to be rather short (1.38 Å). In molecules containing $>N(sp^2)$–aryl (where the aryl group is not *o*-substituted) the coplanarity of the aryl group with the plane formed by the nitrogen and its two substituent atoms is sometimes lost and is thus rarely observed owing to repulsive steric interactions of the *o*-hydrogen atoms with the groups attached to the nitrogen. Such interactions are of lesser importance in cyclodisilazanes because of the smaller angle at the nitrogen atom in the four-membered ring (~ 85 vs. ~ 120°) and the rather long N–Si bonds.

Ortho-Me substitution in the phenyl ring (II) causes a dramatic change in conformation in that the plane of the phenyl ring ends up perpendicular to the plane of the four-membered ring and that the N–C bond is substantially longer (1.42 Å) than in I. Compounds with the *m*- and *p*-Me substituted phenyl rings (III and IV) also adopt the "coplanar" conformation. Bulky phenyl substituents on silicon have no effect on the coplanar conformation of VII.

Crystal packing modes for I, III, IV and VII and the protruding Me (or Ph) groups linked to silicon make it improbable that coplanar conformations result from crystal packing forces. ^{13}C NMR chemical shift data were used to determine the dominant conformations in solution. The additivity of substituent induced chemical shifts for related conformations was assumed for the phenyl ring atoms, by making use of chemical shift data for I and data from the literature. Significant non-additivity ($NA = \delta_{exp} - \delta_{calc}$) values were obtained for II which showed that this molecule in solution is in a conjugation state different from III and IV. Thus conformations determined in solid state are probably dominant ones in solution [3].

Since *NA* values are also affected by steric effects, the *NA* parameter of the *para*-carbon atom in the *N*-phenyl ring is most sensitive to the relative position of the aryl ring with respect to the cyclodisilazane moiety. Moreover, the *para*-carbon atom is on the axis of rotation, therefore its position is unaffected by the rotation of the phenyl group about the N–C bond.

The additivity of the substituent chemical shifts predicted the unexpected coplanar conformation of V, and was corroborated in the crystalline state by X-ray structure analysis [4]. In the coplanar conformation V contains a rather short intramolecular Si ··· Cl contact of 3.14 Å, 0.76 Å shorter than the sum of the Van der Waals radii (3.90 Å). While the existence of a non-bonded Si ··· Cl interaction cannot be ruled out, electronic effects also seem to be present. The results of a joint NMR X-ray study of the VI title compound containing *o*-OMe substituted *N*-phenyl groups, are given in this paper.

Experimental

Synthesis

Bis(*o*-methoxyanilino)dimethylsilane (VIII, b.p. 170–174°C/10^{-2} mbar) was prepared by reaction of the appropriate *o*-methoxyaniline (XI) with dimethyldichlorosilane in diethyl ether, by the method as described by Anderson [8]. Triethylamine was used as the HCl acceptor. The dilithium salt was prepared by the reaction of VIII with butyllithium, and VI was obtained from the dilithium salt with dimethyldichlorosilane [9]. The product was recrystallized from cyclohexane.

Yield: 47%, m.p. 250°C. (Found: C, 6.20; H, 7.11; N, 7.66; Si, 14,98. $C_{18}H_{26}N_2O_2Si_2$ calc: C, 60.30; H, 7.31; N, 7.81; Si, 15.66%); IR (cm^{-1}) 505w, 732m, 800m, 858w, 905m, 960m, 1030s, 1055s, 1120vs, 1180s, 1230s, 1255s, 1275s, 1312vs, 1335vs, 1411m, 1455s, 1465m, 1505vs, 1580m, 1600s; MS *m/e*: 358 ($M^{+\cdot}$, 100%); 343 ($[M-CH_3]^{+\cdot}$, 11%); 328 ($[M-2CH_3]^{+\cdot}$, 31%); 313 ($[M-3CH_3]^{+\cdot}$, 22%); 164 ($M^{2+\cdot}$ and $M^{+\cdot}/2$, 25%).

NMR measurements

^1H, ^{13}C spectra were recorded on a JEOL FX-100 instrument (2.3T) with a turnable probe. Samples were taken in $CDCl_3$ solution and TMS was used as internal standard. ^{13}C multiplicities were verified by attached proton test (APT).

^1H NMR (ppm) 0.43 ($SiCH_3$, s, 12H), 3.68 (OCH_3, s, 6H), 6.5–6.8 (Ar-H, m, 8H).

^{13}C NMR (δ_{TMS} 0.00 ppm) 2.6 ($SiCH_3$, $^1J(^{13}C, ^1H)$: 119.5 Hz), 53.9 (OCH_3, $^1J(^{13}C, ^1H)$: 144.0 Hz), 137.1 C(3), 149.1 C(4), 109.6 C(5), 117.0 C(6), 121.4 C(7), 116.7 C(8) *.

X-ray structure determination

The determination of the unit cell dimensions, space group and the collection of intensity data were performed on a computer-controlled Enraf–Nonius CAD-4 diffractometer at room temperature. Crystal data, data collection and least-squares parameters are listed in Table 1.

* For the numbering of atoms see Fig. 1.

TABLE 1

CRYSTAL DATA, DATA COLLECTION AND LEAST-SQUARES PARAMETERS

Empirical formula	$C_{18}H_{26}Si_2N_2O_2$
M (a.m.u.)	358.6
$F(000)$	768
Crystal dimensions	0.25×0.25×0.40 mm
a (Å)	6.669(1)
b (Å)	18.495(1)
c (Å)	15.968(1)
V (Å^3)	1969.7(3)
Orthorhombic space group	*Pbca*
Z	4
D_x (gcm^{-3})	1.21
λ(Cu-$K_{\bar{a}}$) (Å)	1,5418
μ(Cu-$K_{\bar{a}}$) (cm^{-1})	17.4
2θ limits (°)	3–150
Scan technique	θ–2θ
Reflexions with non-zero intensity	1926
Reflexions used in least-squares (NO)	1743 [$I > 3\sigma(I)$]
Number of variables (NV)	109
Weighting scheme	$4\ F_o^2/\sigma(F_o^2)^2$
R_o	0.042
R_w	0.059
R_{tot}	0.046
$(\Sigma w(\|F_o\| - \|F_c\|)^2/(NO - NV))^{1/2}$	6.00

The structure was solved by the MULTAN program [10] and was refined by full-matrix least-squares for non-hydrogen atoms. At the end of the isotropic refinement an empirical absorption correction was applied [11] (relative transmission coefficients ranged from 0.757 to 1.259 with an average value of 0.989).

Positional parameters of the hydrogen atoms were generated from assumed geometries and checked in difference maps. No hydrogen parameters were refined.

TABLE 2

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

Atom	x/a	y/b	z/c	B(eq)
Si	5818.8(7)	149.2(2)	715.2(3)	3.08(1)
O	2022(2)	−1397.6(8)	−648.5(8)	4.80(6)
N	4242(2)	−515.2(8)	285.9(9)	3.34(5)
C(1)	8211(3)	−246(1)	1080(1)	4.74(9)
C(2)	4513(3)	654(1)	1558(1)	4.80(9)
C(3)	3238(2)	−1089.2(9)	667(1)	3.15(6)
C(4)	2019(2)	−1552(1)	194(1)	3.67(7)
C(5)	953(3)	−2107(1)	562(1)	4.46(8)
C(6)	1074(3)	−2215(1)	1416(1)	4.87(9)
C(7)	2289(3)	−1781(1)	1892(1)	4.61(8)
C(8)	3364(3)	−1230(1)	1525(1)	3.84(7)
C(9)	791(4)	−1810(1)	−1187(1)	6.7(1)

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

For the scattering factors used see Ref. 4. The final atomic parameters of the non-hydrogen atoms are given in Table 2 *.

Discussion

NMR results

In the preceding papers [3,4] we have shown that aromatic ^{13}C chemical shift non-additivity (*NA*) data differ for coplanar and perpendicular conformations. While absolute *NA* values for the ring carbon atoms of III and IV are much lower than 1 ppm (these are practically strain-free systems), there are significantly higher *NA* parameters in II and V. High *NA* values for atoms C(3), C(4) and C(8) (II) or C(4) (V), on the other hand, may be attributable rather to steric compression effects than to differences in conjugation. Steric effects therefore should be taken into account in the analysis by choosing suitable model compounds such as *o*-toluidine (IX) for II and *o*-chloroaniline (X) for V. The high *NA* value (−6.5) for the C(6) atom in the *p*-position in II (IX: 2.1) and the low *NA* value (0.5) for C(6) in V (X: 1.2) clearly indicates that II is in a conjugation state markedly different from I, III, IV, V, IX and X.

An identical procedure was followed in the present case. Table 3 lists the *NA* parameters of VI and *o*-methoxyaniline (XI). *NA* values for C(6) are comparable: −2.4 (VI) and −3.0 (XI) from which a similar state of conjugation (and conformation) may be inferred.

Equally high *NA* parameters were obtained for C(5) (−5.6 (VI) and −5.8 (XI)) though this value is rather low for all the other compounds investigated; typically in the range of 0.2–0.7. These high values may be associated with steric interactions between C(5) and the methyl group in the −OMe moiety lying in the plane of the phenyl ring in the crystal (cf. close contacts listed in Table 4).

The description of the crystal structure

Crystals of VI have the coplanar conformation (Fig. 1). The dihedral angle formed by the best plane of the phenyl ring and the cyclodisilazane ring is 7.4(1)°, the N–C bond distance is 1.395(2) Å (bond lengths and angles are given in Table 4). The methyl group of the −OMe moiety lying in the plane of the phenyl ring forms several close contacts with C(5)–H(5) (cf. Table 4).

The coplanar conformation results in a rather short Si · · · O intramolecular non-bonded distance of 2.733(2) Å. The vector drawn from Si to O closes a fairly planar five membered ring $\overline{SiNC{=}CO}$. The "endocyclic" angles in this ring at the N, C(3) and C(4) atoms are always smaller than the "exocyclic"ones (Fig. 2). The differences in angles are 2.9° (N), 2.2 (C(3)) and 11.3° (C(4)). These angular distortions tend to shorten the Si · · · O distance.

The molecular structure of VI seems to be analogous to organosulphur molecules exhibiting short S · · · O non-bonded interactions. Such interactions, beside determining the conformation of the molecules, also influence their chemical and spectroscopic behaviour (c.f. [12,13] and references therein). S · · · O non-bonded interactions may be regarded as a nucleophilic attack of oxygen on the sulphur

* Lists of observed and calculated structure factors, anisotropic temperature parameters and calculated hydrogen positional parameters can be obtained from the authors.

TABLE 3

NA PARAMETERS (ppm) FOR VI AND XI

Compound	C(3) [a]	C(4)	C(5)	C(6)	C(7)	C(8)
VI	5.2	−0.2	−5.6	−2.4	−0.5	−0.2
XI	3.8	1.6	−5.8	−3.0	−0.7	−0.4

[a] For the numbering of atoms see Fig. 1.

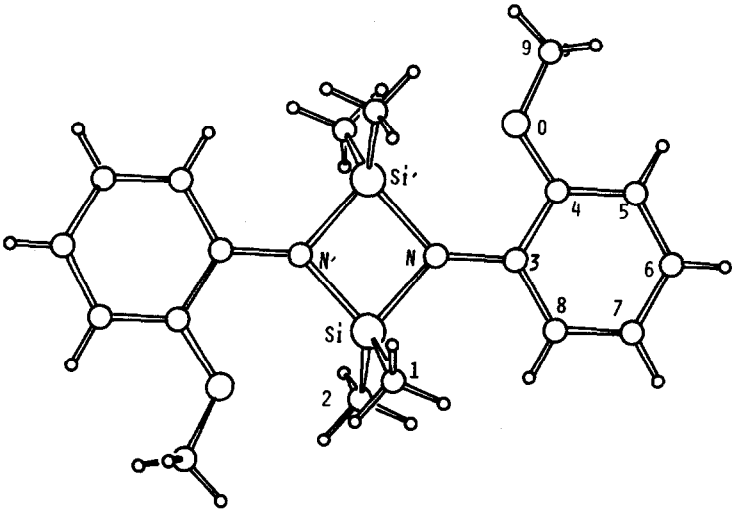

Fig. 1. The molecular structure of VI showing the numbering of atoms.

TABLE 4

BOND LENGTHS AND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond lengths (Å)					
Si–N	1.757(2)	O–C(4)	1.375(2)	C(3)–C(8)	1.397(3)
Si–N′	1.737(2)	O–C(9)	1.413(3)	C(4)–C(5)	1.380(3)
Si–C(1)	1.849(2)	N–C(3)	1.395(2)	C(5)–C(6)	1.381(4)
Si–C(2)	1.855(2)	C(3)–C(4)	1.402(3)	C(6)–C(7)	1.371(3)
				C(7)–C(8)	1.377(3)
Bond angles (°)					
N–Si–C(1)	111.3(2)	C(4)–O–C(9)	118.8(3)	O–C(4)–C(3)	113.6(3)
N–Si–C(2)	110.8(2)	Si–N–C(3)	130.5(2)	O–C(4)–C(5)	124.9(3)
N–Si–N′	84.2(1)	Si–N–Si′	95.8(1)	C(3)–C(4)–C(5)	121.5(3)
C(1)–Si–C(2)	112.0(2)	C(3)–N–Si′	133.4(2)	C(4)–C(5)–C(6)	119.9(3)
C(1)–Si–N′	117.7(2)	N–C(3)–C(4)	120.5(3)	C(5)–C(6)–C(7)	119.8(4)
C(2)–Si–N′	117.4(2)	N–C(3)–C(8)	122.7(3)	C(6)–C(7)–C(8)	120.3(4)
		C(4)–C(3)–C(8)	116.7(3)	C(3)–C(8)–C(7)	121.6(3)
Selected intramolecular non-bonded distances (Å) and angles (°)					
Si · · · Si′	2.591(1)	N · · · N′	2.343(2)	Si′ · · · O	2.723(2)
C(5) · · · H(9c)	2.78	C(9) · · · H(5)	2.56		
O · · · Si′–N′	153.4(1)	O · · · Si′–N	69.3(1)	Si · · · O–C(4)	102.4(3)

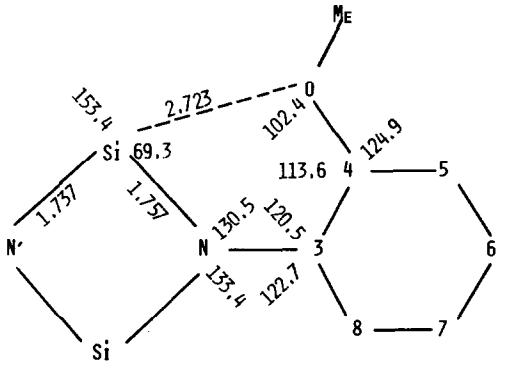

Fig. 2. A schematic diagram of part of the molecule indicating some important geometrical data.

atom. The close S · · · O approach is achieved by the formation of a quasi-linear Y–S · · · O moiety (where Y is an electron withdrawing or polarizable "counter atom" [14]) favourable for HOMO-LUMO and coulombic interactions. No linear arrangement of atoms in VI (Y=N) can be achieved since nitrogen and silicon are part of a four-membered ring, though the angle of 153.4° seems to be large enough for Si · · · O interaction. The main difference between Si · · · O and S · · · O interactions of this type is the nature of the oxygen atom; which in VI is an ether oxygen, and in S · · · O interactions is a double-bonded oxygen (carbonyl or nitro group).

Silicon is more electrophilic than sulphur ($\chi_{Si} = 1.8$, $\chi_S = 2.5$) and readily interacts with weaker nucleophiles such as the oxygen in ether or chlorine. The differences in electronegativity, $\Delta\chi_{Si,Cl} = 1.2$, $\Delta\chi_{S,Cl} = 0.5$, $\Delta\chi_{Si,O} = 1.7$ and $\Delta\chi_{S,O} = 1.0$ suggest that silicon interactions (Si · · · O or Si · · · Cl) may be stronger than those of sulphur. There are a number of molecules which exhibit quite strong Si · · · O interactions (e.g. [(*N*-chlorodimethylsilylacetamido)methyl]dimethylsilane, Si · · · O: 1.92 Å [15] or (aryloxymethyl)trifluorosilanes, Si · · · O: 1.94–2.08 Å [16].

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