Journal of Organometallic Chemistry, 398 (1990) 59–64
Elsevier Sequoia S.A., Lausanne
JOM 21102

Synthesis and crystal structure of the crowded disiloxane $[\{(Me_3Si)_3C\}Cl_2Si]_2O$

Colin Eaborn *, Peter B. Hitchcock, Paul D. Lickiss * and Alan D. Taylor
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (UK)

(Received May 16th, 1990)

Abstract

The disiloxane $(TsiCl_2Si)_2O$ (Tsi = $(Me_3Si)_3C$) has been prepared from TsiLi and $(Cl_3Si)_2O$. An X-ray diffraction study has revealed extensive disorder in the crystal, and although the data favour a linear Si–O–Si arrangement, with fully staggered Tsi groups, an alternative interpretation involving a bent structure, with an Si–O–Si angle of 139.5(1)°, cannot be completely ruled out. It is suggested that crystals of the related disiloxane $(TsiF_2Si)_2O$, diffraction data for which were previously erroneously interpreted by others, show the same disorder, and that the two disiloxanes are isomorphous.

Introduction

During systematic studies of compounds containing the very bulky tris(trimethylsilyl)methyl group, $(Me_3Si)_3C$ (sometimes denoted below by Tsi) [1] we made the disiloxane $[(Me_3Si)_3CSiCl_2]_2O$, **1**, and decided to determine its crystal structure since the magnitude of the Si–O–Si angle in disiloxanes is known to be sensitive to electronic and steric influences [2,3]. The structural determination proved to present an unusual crystallographic problem.

Results and discussion

Compound **1** was made by treating $(Cl_3Si)_2O$ with a 2 molar proportion of TsiLi in tetrahydrofuran–diethyl ether.

A feature of interest is that whereas the ^1H NMR spectrum of **1** at 35 °C (in CCl_4) shows only one singlet, at δ 0.40, that at -90 °C (in CD_2Cl_2) contains clear

---

* Present address: Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Great Britain.

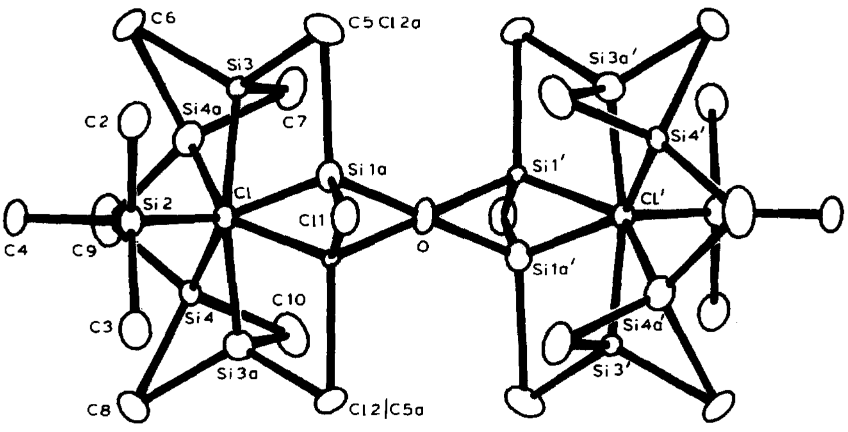

Fig. 1. Atom positions, shown as 20% thermal ellipsoids, with numbering, in the disordered structure of $(TsiCl_2Si)_2O$.

singlets, at δ 0.390, 0.330, 0.264, and 0.217, in height ratios of ca. 1.9/3.4/1.9/3.1. The origin of such effects in tris(trimethylsilyl)methyl derivatives has been discussed previously [4].

Like $TsiSiCl_3$ [5], **1** is very unreactive for a chlorosilane.

A single crystal X-ray diffraction study revealed the presence of disorder in the crystal, as can be seen from Fig. 1, which is compatible with two interpretations. For each $(Me_3Si)_3CSiCl_2$ group there are alternative sites for three of the silicon atoms, namely that bearing the chlorine substituents and two of those in the Me_3Si groups. Initially the alternative sites were assumed to have equal occupancies. The carbon atoms of the Me groups in the two Me_3Si ligands involved in disorder occupy overlapping positions and were refined as single sites of occupancy 1.0. In two locations a Cl and a methyl C atom also overlap, and these were refined as single sites of occupancy (0.5 Cl + 0.5 C). Figure 1 shows the results of this refinement with the atoms represented as 20% thermal vibration ellipsoids. The set of atoms positions lies across the crystallographic inversion center and has non-crystallographic $2/m$ symmetry. This disordered model could be interpreted in two ways. In one of these the molecule would be that formed from Si1, Si2, Si3 and Si4 on the left hand side of the Figure and Si1′, Si2′, Si3′, and Si4′ on the right hand side. This would give a linear Si–O–Si arrangement in a molecule of $\bar{1}$ symmetry, with the Tsi groups in fully staggered positions. Combined with the equivalent molecule related by reflection through the plane containing Si2, Cl, O, Cl′, and Si2′, this would generate the observed data. The other possibility is that the actual molecule is that formed from Si1, Si2, Si3, and Si4 on the left hand side, and Si1a′, Si2′, Si3a′, and Si4a′ on the right hand side. This would give a bent Si–O–Si arrangement (with the very plausible Si–O–Si angle of 139.5(1)°) in a molecule of symmetry 2 (again with the Tsi group in staggered positions). Taken together with the equivalent molecule related by the non-crystallographic mirror plane, as before, this would give rise to the observed data.

However, inspection of the thermal ellipsoids of the Si atoms in Fig. 1 shows that those for Si1, Si3, and Si4 are slightly but systematically smaller than those for Si1a, Si3a, and Si4a. Since the vibrations of the Si atoms at the two ends of the molecule

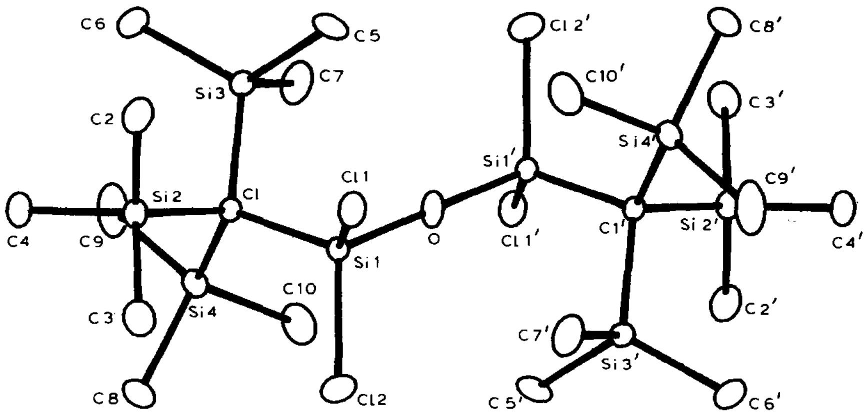

Fig. 2. The favoured molecular structure of $(TsiCl_2Si)_2O$, with atom numbering.

should be identical, this argues strongly against the bent structure, and suggested to us that the molecule has linear Si–O–Si bonding (see Fig. 2) and that there is slightly unequal occupancy of the two component molecules of the disorder.

A refinement of the occupancies of the two sets of Si atom positions gave values of 0.58 for Si1, Si3, and Si4, and 0.42 for Si1a, Si3a, and Si4a. The occupancies of the mixed sites Cl2/C5a and C4/Cl2a were adjusted accordingly. The refinement converged at $R = 0.050$, $R' = 0.072$ (see Experimental Section).

Because of the disorder, detailed analysis of the structural parameters for **1** (see Table 1) would be unjustified, but there are a few seemingly significant features. First, the C–$SiMe_3$ bonds within the Tsi groups show the usual lengthening (mean 1.94(2) Å), and the C–$SiCl_2O$ bond is distinctly shorter (1.841(4) Å). Secondly, the Si–O bond lengths (mean 1.686(6) Å) fall outside the range (1.589 to 1.645(6) Å) listed for 23 disiloxanes in a recent survey [2]. (The corresponding bond length in $Cl_3SiOSiCl_3$, as determined by electron diffraction, is 1.592(10) Å [6]). Finally, the Cl–Si–Cl angle (102.7(1)°) is well below the tetrahedral value, presumably to relieve the steric interaction with the Me_3Si groups.

We should emphasize that although the evidence favours the linear structure, the bent structure cannot be completely ruled out.

During the course of this study [7] a report appeared on the crystal structure of the closely related disiloxane $(TsiF_2Si)_2O$ in which it was concluded that the molecule was linear [8]. However a clearly erroneous model was chosen for the disorder, which resulted in some impossibly short intramolecular non-bonded contacts, and the structure is recorded in the files of the Cambridge Crystallographic Data Centre as being in error. We think it very likely that the disorder is in fact the same as that we observe, and that the structures are essentially isomorphous, as suggested by the similarity in the unit cell dimensions. (For **1**: $a = 8.998(2)$, $b = 12.669(3)$, $c = 15.849(3)$ Å, $\beta = 92.62(2)°$; for $TsiF_2SiOSiF_2Tsi$: $a = 9.084(2)$, $b = 12.226(2)$, $c = 15.692(3)$ Å, $\beta = 90.87(2)°$.)

Experimental

Preparation of $(TsiCl_2Si)_2O$, 1

A solution of TsiLi was made [9] from TsiH (5.0 g, 0.021 mol) in tetrahydrofuran (THF) (20 cm^3) and MeLi (20 cm^3 of 1.35 *M* solution in Et_2O made from MeCl and

Table 1

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses [a]

(a) *Bonds*			
C1–Si1	1.841(4)	C1–Si2	1.955(4)
C1–Si3	1.948(4)	C1–Si4	1.918(4)
Si1–Cl1	2.027(2)	Si1–Cl2	2.070(2)
Si1–O	1.680(2)	Si1–C1	1.841(4)
Si2–C1	1.955(4)	Si2–C2	1.877(5)
Si2–C3	1.882(5)	Si2–C4	1.882(5)
Si3–C1	1.948(4)	Si3–C5	2.105(3)
Si3–C6	1.851(6)	Si3–C7	1.959(6)
Si4–C1	1.918(4)	Si4–C8	1.907(6)
Si4–C9	1.981(7)	Si4–C10	1.895(6)
Si1a–Cl1	2.037(3)	Si1a–O	1.693(2)
Si1a–C1	1.825(5)	Si1a–Cl2a	2.088(3)
Si3a–C5a	2.182(4)	Si3a–C1	1.954(5)
Si3a–C8	1.830(6)	Si3a–C10	1.988(6)
Si4a–C1	1.931(5)	Si4a–C6	1.935(6)
Si4a–C7	1.910(6)	Si4a–C9	2.024(6)
C1–Si3a	1.954(5)	C1–Si4a	1.931(5)
C1–Si1a	1.825(5)		
(b) *Angles*			
Si1–C1–Si2	109.5(2)	Si1–C1–Si3	109.4(2)
Si1–C1–Si4	111.5(2)	Si2–C1–Si3	106.8(2)
Si2–C1–Si4	109.5(2)	Si3–C1–Si4	110.0(2)
Cl1–Si1–Cl2	102.7(1)	Cl1–Si1–O	103.1(1)
Cl1–Si1–C1	112.2(1)	Cl2–Si1–O	112.2(1)
Cl2–Si1–C1	109.9(2)	O–Si1–C1	115.9(2)
C1–Si2–C2	114.1(2)	C1–Si2–C3	113.4(2)
C1–Si2–C4	111.4(2)	C2–Si2–C3	105.8(2)
C2–Si2–C4	105.1(2)	C3–Si2–C4	106.4(2)
C1–Si3–C5	103.3(2)	C1–Si3–C6	114.5(2)
C1–Si3–C7	107.6(2)	C5–Si3–C6	117.2(2)
C5–Si3–C7	111.5(2)	C6–Si3–C7	102.7(3)
C1–Si4–C8	112.6(2)	C1–Si4–C9	107.9(2)
C1–Si4–C10	110.6(2)	C8–Si4–C9	111.0(3)
C8–Si4–C10	102.6(3)	C9–Si4–C10	112.2(3)
Si1a–C1–Si3a	109.5(2)	Si1a–C1–Si4a	110.6(2)
Si3a–C1–Si4a	110.1(2)	Si2–C1–Si4a	110.0(2)
Si2–C1–Si1a	110.5(2)	Si2–C1–Si3a	106.1(2)
Cl1–Si1a–O	102.2(1)	Cl1–Si1a–C1	112.4(2)
Cl1–Si1a–Cl2a	102.5(1)	O–Si1a–C1	116.1(2)
O–Si1a–Cl2a	114.2(1)	C1–Si1a–Cl2a	108.5(2)
C5a–Si3a–C1	101.4(2)	C5a–Si3a–C8	119.3(2)
C5a–Si3a–C10	114.1(2)	C1–Si3a–C8	114.4(3)
C1–Si3a–C10	105.3(3)	C8–Si3a–C10	101.9(3)
C1–Si4a–C6	111.6(2)	C1–Si4a–C7	110.3(3)
C1–Si4a–C9	105.7(3)	C6–Si4a–C7	101.4(3)
C6–Si4a–C9	112.9(3)	C7–Si4a–C9	115.0(3)
Si1–O–Si1′	180		

[a] Symmetry element ′ is $-x, -y, -z$.

Li), and a solution of $(Cl_3Si)_2O$ (3.0 g, 0.010 mol) in dry THF (15 cm^3) was added dropwise. The mixture was heated under reflux for 2 h and the solvents were removed under vacuum to leave a sticky solid, which was extracted three times with hexane. The combined extracts were filtered, most of the solvent was evaporated off, and the remaining solution kept for 2 weeks at $-10\,^\circ$C. The colourless crystals that had separated were filtered off and shown to be 1,3-bis[tris(trimethylsilyl)methyl]tetrachlorodisiloxane (1.1 g, 15.5%), m.p. $> 350\,^\circ$C. (Found : C, 35.8; H, 7.7. $C_{20}H_{54}Cl_4OSi_8$ calcd: C, 35.5; H. 7.9%); δ_H (CCl_4) 0.40 (s) at $35\,^\circ$C (at $-90\,^\circ$C there were singlets at δ 0.39, 0.33, 0.265, and 0.217); ν(SiOSi) (in CCl_4) br 1010–1090 cm^{-1}; m/z (CI, NH_3) 694, ($[M + NH_4]^+$).

Details of structural determination

Crystal data. $C_{20}H_{54}OCl_4Si_8$, $M = 677.2$, monoclinic, space group $P2_1/n$, $a = 8.998(2)$, $b = 12.669(3)$, $c = 15.849(3)$ Å, $\beta = 92.62(2)^\circ$, $U = 1804.8$ Å^3, $Z = 2$, $D_c = 1.25$ gcm^{-3}, $F(000) = 724$. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 6.0$ cm^{-1}.

Data were collected from a crystal of dimensions ca. $0.4 \times 0.15 \times 0.15$ mm (formed from hexane at $-10\,^\circ$C as described above) on an Enraf–Nonius CAD4 diffractometer in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35 \tan\theta)^\circ$ and a maximum scan time of one minute. A total of 3327 unique reflections were measured for $2 < \theta < 25^\circ$ and $+h + k \pm l$, and 2086 reflections with $|F^2| > 3\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.041I)^2\}^{1/2}/\mathrm{Lp}$. There was no crystal decay during the data collection.

The structure was solved by direct methods by use of the MULTAN program [10] and refined by full matrix least squares with non-hydrogen atoms anisotropic. Details of the disorder and of the way in which it was interpreted are given in the

Table 2

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$)

	x	y	z	U_{eq} [a]
Si1	900(2)	433(1)	−839(1)	29(1)
Si2	654(1)	1657(1)	−2535(1)	39(1)
Si3	−2017(2)	1618(2)	−1333(1)	33(1)
Si4	910(2)	2885(2)	−797(1)	39(1)
Cl1	814(1)	−824(1)	−1630(1)	45(1)
Cl2/C5a	3160(2)	607(2)	−572(1)	68(1)
O	0	0	0	44(2)
C1	147(4)	1637(3)	−1349(2)	28(2)
C2	−566(6)	797(4)	−3238(3)	59(3)
C3	2618(5)	1224(5)	−2707(3)	60(3)
C4	459(6)	3021(4)	−2997(3)	57(3)
C5/Cl2a	−2540(2)	5(2)	−1465(1)	54(1)
C6	−2964(5)	2543(4)	−2085(3)	56(3)
C7	−2573(6)	2164(5)	−235(3)	73(3)
C8	2854(6)	3245(4)	−1133(4)	64(3)
C9	−512(9)	4049(4)	−1047(4)	85(4)
C10	1216(7)	2648(5)	378(3)	76(3)
Si1a	−355(3)	304(2)	−1029(2)	26(1)
Si3a	1935(3)	2089(2)	−702(2)	41(1)
Si4a	−1465(3)	2607(2)	−1172(2)	38(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Discussion above. In the final refinement two sets of hydrogen atoms were included at fixed calculated positions with occupancies corresponding to those of the two Si atom sites, and with a common isotropic temperature factor of B of 8.0 Å^2. Refinement with a weighting scheme of $w = 1/\sigma^2(F)$ converged at residuals of $R = 0.050$, $R' = 0.072$. Programs from the Enraf–Nonius SDP-Plus package were run on a MicroVAX computer. Atom coordinates for non-hydrogen atoms are shown in Table 2. Tables of hydrogen atoms positions, thermal vibration parameters, and structure factors are available from the authors.

Acknowledgements

We thank the S.E.R.C. for the support of this work and the award of a Research Studentship (to ADT), Dow Corning Ltd for their support under the CASE programme, and The Royal Society for the award to PDL of a 1983 University Research Fellow.

References

1 See, e.g., C. Eaborn in H. Sakurai (Ed.), Organosilicon and Bioorganosilicon Chemistry, Ellis Horwood, Chichester, 1985, pp. 123–130.

2 E. Lukevics, O. Pudova, and R. Sturkovich, Molecular Structure of Organosilicon Compounds, Ellis Horwood, Chichester, 1989, pp. 191–192.

3 W.S. Sheldrick in S. Patai and Z. Rappoport (Eds.), The Chemistry of Organosilicon Compounds, Wiley, Chichester, 1989, pp. 262–266.

4 A.G. Avent, P.D. Lickiss, and A. Pidcock, J. Organomet. Chem., 341 (1988) 281; N.H. Buttrus, C. Eaborn, M.N.A. El-Kheli, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, and K. Tavakkoli, J. Chem. Soc., Dalton Trans., (1988) 381.

5 S.S. Dua, C. Eaborn, D.A.R. Happer, S.P. Hopper, K.D. Safa, and D.R.M. Walton, J. Organomet. Chem., 178 (1979) 75.

6 W. Airey, C. Glidewell, A.G. Robiette, and G.M. Sheldrick, J. Mol. Struct., 8 (1971) 413.

7 A.D. Taylor, D. Phil. Thesis, University of Sussex, 1988.

8 U. Klingebiel, S. Pohlmann, L. Skoda, C.L. Lensch, and G.M. Sheldrick, Z. Naturforsch. B, 40 (1985) 1023.

9 Z.H. Aiube and C. Eaborn, J. Organomet. Chem., 269 (1984) 217.

10 G. Germain, P. Main, and M.M. Woolfson, Acta Crystallogr. A, 27 (1971) 368.